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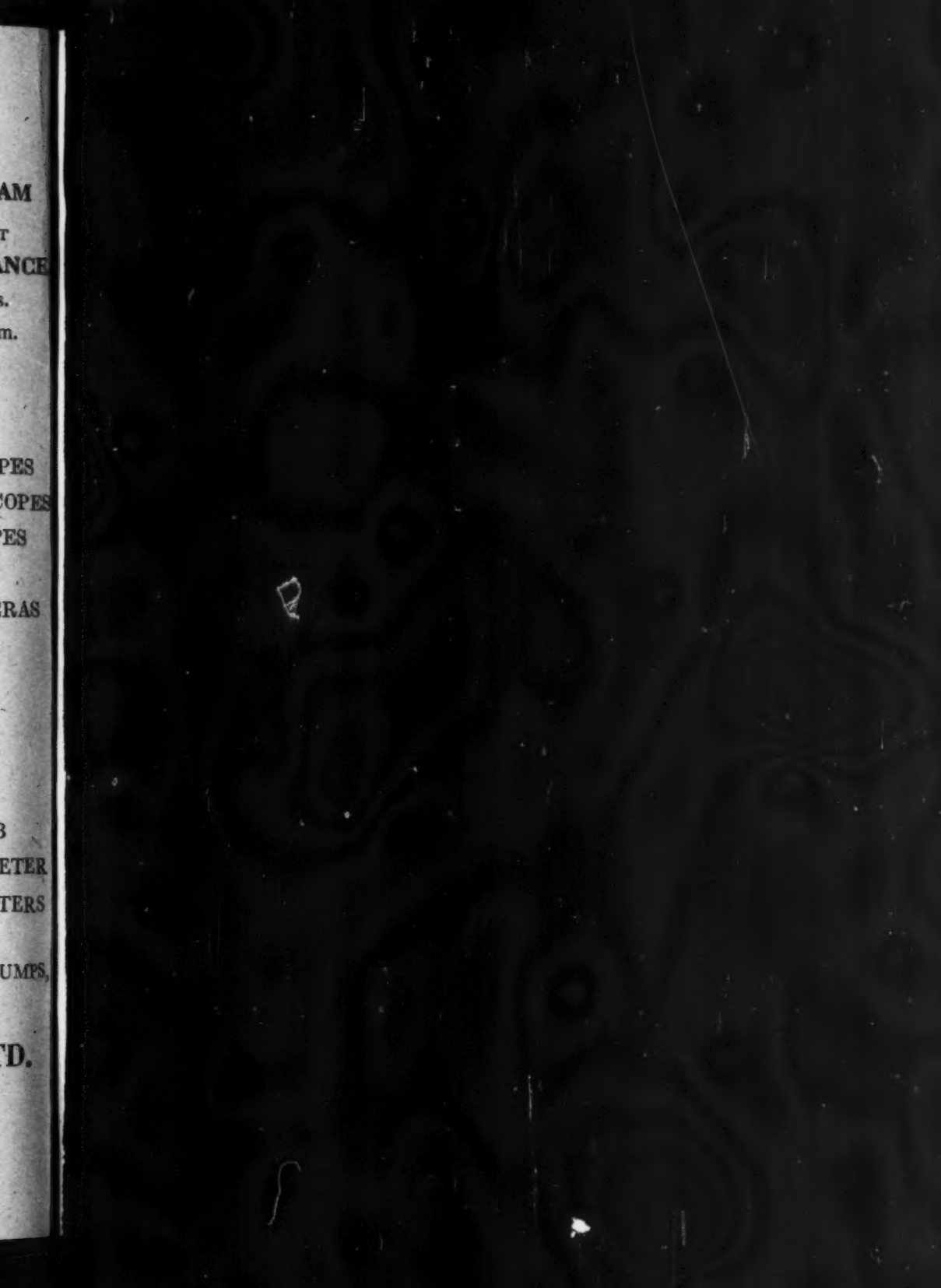

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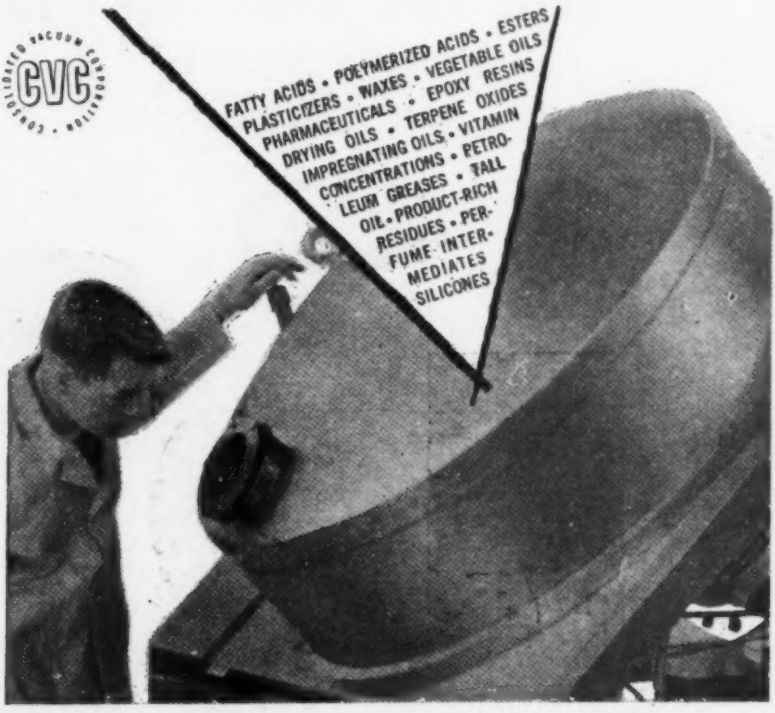

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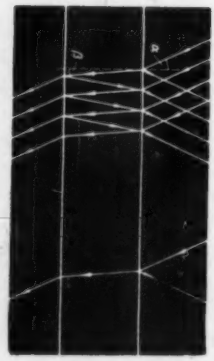

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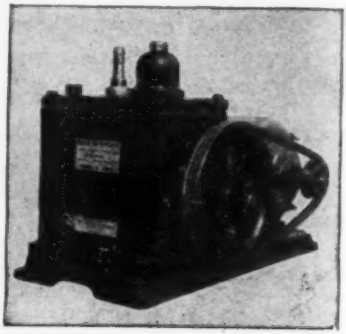

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[Jour. Indian Chem. Soc., Vol. 38, No. 11, 1961]

Electrometric Studies on the Precipitation of Hydrous Oxides of Some Quadrivalent Cations. Part I. Precipitation of Zirconium Hydroxide from Solutions of Zirconium Salts

R. P. Singh and N. R. Banerjee

The precipitation of basic salts and hydroxide of zirconium from solutions of its sulphate, oxychloride, and nitrate has been studied. Conductometric and *p*H titrations of the salt solutions with sodium hydroxide show that the precipitated hydroxide contains appreciable quantities of the anions. Compositions of the basic salts, thus obtained, have been deduced from the titration curves. Hydrolysis of these salts have been found to be a slow process. The increasing order of anion penetration is the same as the co-ordinating power of the respective anions, viz., nitrate, chloride, and sulphate.

Titrations of zirconium sulphate solutions against baryta show that the initially precipitated basic sulphate gives up the anion gradually with little change in the *p*H or the conductance and the ultimate product consists of almost pure hydroxide.

The mechanism of precipitation of the hydroxides of quadrivalent cations (Zr^{4+}, Hf^{4+}, Th^{4+}) by alkalies has been little studied. Evidence for the formation of zirconates (Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35,** 847) as well as its contradiction (Britton, *J. Chem. Soc.*, 1925, 2120) is found in literature. Chauvenet (*Ann. chim. phys.*, 1920, *ix*, **13,** 82) titrated zirconium sulphate solutions conductometrically and from the titration curves he inferred the formation of basic sulphates of the formulas $ZrOSO_4$ and $ZrOSO_4$, ZrO_2. Britton (*loc. cit.*) could not confirm these contentions from *p*H titrations. Adolf and Pauli (*Kolloid Z.*, 1921, **29,** 172) found that hydrolysis of solutions of zirconium oxychloride of concentrations between $0.0022M$ and $0.125M$ varied irregularly on standing. Britton (*loc. cit.*), on the basis of potentiometric titrations of different zirconium salt solutions, suggested the presence of an equilibrium mixture of a basic salt and free acid in aqueous solutions of these salts. On addition of alkali, the free acid is supposed to be neutralised with the consequent precipitation of the basic salt. No work appears to have been done on zirconium nitrate on these lines. In view of the difference of opinion regarding the composition of the basic salts, it was considered worthwhile to reinvestigate these equilibria.

EXPERIMENTAL

Procedure

A freshly prepared solution of the zirconium salt (10 c.c.) was taken in a vessel (kept in a thermostat at 25°) in which a current of nitrogen was passed during titration. Sodium hydroxide or baryta solution was added from a microburette and conductance or *p*H readings were taken after each addition of alkali.

Subsequently 10 c.c. of the solution was taken in each of several pyrex bottles. The air in the bottles was displaced by nitrogen and increasing quantities of the standard alkali were added to each of them. The bottles were shaken from time to time and conduc-

tance and *p*H readings of the mixtures were taken in each case after an interval of 3 days. On keeping the bottles for a longer period, the conductance and *p*H readings remained unchanged, showing attainment of equilibrium during this period. These will henceforth be referred to as equilibrium (bottle) titrations.

For measurements of *p*H, a Beckman *p*H meter (model H-2) was used; for measurements of conductance, a conductivity bridge (Serfass, model RCM 15) was used.

Zirconium Sulphate

The composition of L.R., B. D. H. sample of zirconium sulphate used was determined by analysis as $Zr(SO_4)_2,0.025H_2SO_4,3.9\ H_2O$. This sample of zirconium sulphate (0.401 g.) was dissolved in water and 1.0299 N-H_2SO_4 (5 c.c.) was added to it to prevent hydrolysis. The volume was made to 250 c.c. A 0·176N-solution of carbonate-free NaOH and a 0.175N solution of baryta were used for the titrations.

Precipitation with NaOH.—The results of continued and equilibrium *p*H titrations against 0.176N-NaOH at 25° are recorded in Fig. 1.

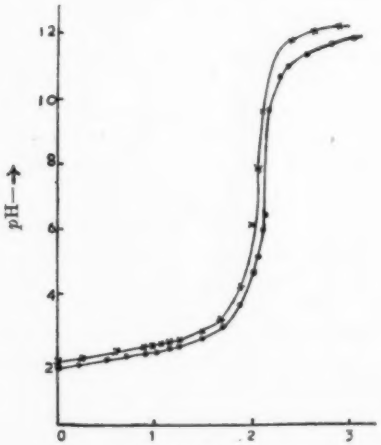


FIG. 1
×—Contd. titration.
●—Bottle „

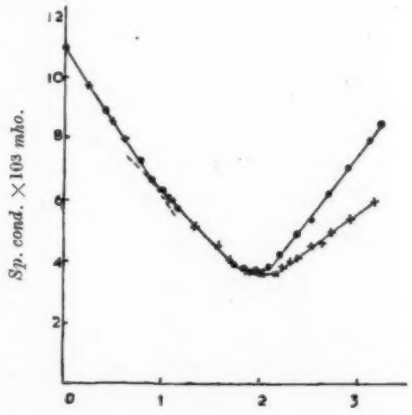


FIG. 2
●—Contd. titration.
×—Bottle „

The volume of NaOH needed for neutralisation of free H_2SO_4 in 10 c.c. of the zirconium sulphate solution would be 1.17 c.c. Assuming that pure zirconium hydroxide is precipitated afterwards, the amount of sodium hydroxide required for this purpose would be 1.03 c.c. Total volume of alkali needed should then be 2.2. c.c.

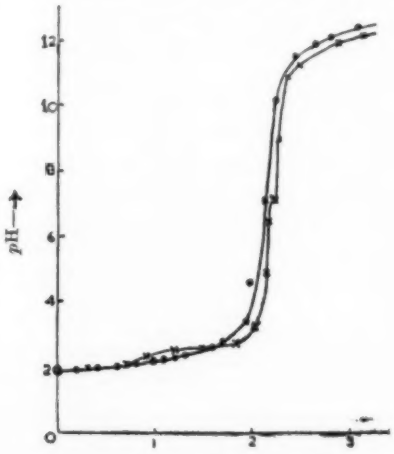
The neutralisation curve shows that in the continued titration there is at first a flat portion showing the gradual neutralisation of free sulphuric acid. This is followed by a steep rise, the inflection occurring when 2.01 c.c. of alkali had been added. At this stage, the calculated composition of the precipitate was ZrO_2, $0.36SO_3$. Britton (*loc. cit.*) had

reported that this inflection occurred when three equivalents of alkali had been added. Further addition of alkali was reported to cause partial decomposition of the precipitate even beyond the stage when the composition of the precipitate corresponded with the formula $ZrO_2,0.16SO_3$.

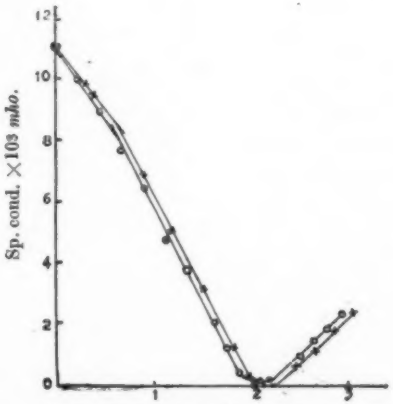
Our results of equilibrium titration show that hydrolysis of zirconium sulphate is a slow reaction. The inflection occurs at 2.13 c.c. and the calculated composition of the precipitate corresponds to the formula $ZrO_2,0.14SO_3$. The remaining acid was not extracted from the basic salt even by contact with the alkali for more than 72 hours.

The results of conductometric titrations of zirconium sulphate against sodium hydroxide are shown in Fig. 2. In the continued and in equilibrium titrations, the first breaks occurred when 0.8 c.c. of alkali had been added. The solution became opalescent and precipitation began at this stage. This was followed by a regular fall in conductance and then a rounded portion corresponding to the attack of the basic salt by the alkali. The rounded portion was followed by a straight line denoting a sharp rise in conductance produced by the free alkali. The end points obtained by drawing tangents to the curves show that the volumes of the alkali consumed in the continued and equilibrium titrations are 2.03 c.c. and 2.13 c.c. respectively, thus corroborating the results obtained by *p*H titrations.

Precipitation with Barium Hydroxide.—Use of barium hydroxide is more advantageous in the study of metallic sulphates because it not only neutralises the acid obtained by hydrolysis, but also precipitates an equivalent amount of barium sulphate, thus producing sharper breaks in the conductivity curves (Harned, *J. Amer. Chem. Soc.*, 1917, **39**, 254).



$Ba(OH)_2$ (*c.c.*).
FIG. 3
●—Contd. titration.
×—Bottle ,,



$Ba(OH)_2$ (*c.c.*).
FIG. 4
●—Contd. titration.
×—Bottle ,,

Our results of *p*H titrations with baryta (Fig. 3) show that more of alkali is consumed both in continued as well as equilibrium titrations (2.13 c.c. and 2.2 c.c. respectively). It is interesting to note that in equilibrium titrations, the amount of alkali consumed corresponds to what would be required for the precipitation of pure zirconium hydroxide,

a fact which has been further confirmed by conductometric titrations (Fig. 4), the latter showing some interesting features. The general appearance of the curves of continued and equilibrium titrations being similar, only the latter will be discussed. The initial decrease in conductance corresponds to neutralisation of free sulphuric acid. Beginning of precipitation of zirconium hydroxide is marked by a break which is not very pronounced. After this, the curve becomes more steep, probably because not only the acid is neutralised by the alkali, but zirconium ions are also precipitated. When 2.0 c.c. of alkali had been added, conductance became practically zero, indicating that practically all ions had been removed from the solution, or in other words, precipitation of zirconium and sulphate ions was complete. The conductance did not rise during the addition of the next 0.2 c.c. of barium hydroxide, indicating that this much of baryta was taken up by the precipitate in some way. As the precipitate consisted of basic zirconium sulphate, addition of baryta must be responsible for its conversion into zirconium hydroxide, barium sulphate being formed simultaneously. All these products being insoluble, conductance does not rise during this stage.

The above results can also be explained satisfactorily by the application of phase rule to the system. Addition of barium hydroxide in the initial stages causes precipitation of the basic sulphate according to the equation:

$$X\ Zr(SO_4)_2 + Y\ Ba(OH)_2 = Zr_x(SO_4)_{2x-y}(OH)_{2y} + Y\ BaSO_4.$$

While the precipitation of the basic sulphate proceeds, there are four phases in the system, viz., water vapour, solution, basic zirconium sulphate, and barium sulphate. Under these conditions, the number of components is four, one of which is water, the remaining being any three of the four independent species shown in the above equation. According to the phase rule, the system can then possess two degrees of freedom. These apparently are temperature and pressure. But on addition of a slight excess of baryta beyond the stage, when precipitation of zirconium as basic sulphate is complete, a new phase, *i.e.*, pure zirconium hydroxide, makes its appearance. The number of degrees of freedom is thereby reduced to unity. The temperature of the system during these titrations having been maintained constant, the only degree of freedom is lost and the system becomes non-variant as shown by the flat portions in the titration curves which show the constancy of the property (conductance) of the system. The results of *p*H titrations in this region are similar to those of conductometric titrations, as shown by curves in Fig. 5 which depict the results of titrations in which 25 c.c. of the same zirconium sulphate solution was used instead of 10 c.c. as in other titrations.

Zirconium Oxychloride

0.02*M* Aqueous solutions of Merck's G.R. zirconium oxychloride were titrated against 0.3875*N*-NaOH. The solutions were clear but acidic owing to hydrolysis. The first portion of the continued *p*H titration curve (Fig. 6) shows that the free acid is gradually neutralised by alkali, leaving basic zirconium chloride. The inflection occurs when 0.96 c.c. of alkali has been added. The composition of the basic salt therefore corresponds to the formula $Zr(OH)_{3\cdot86}Cl_{0\cdot14}$. Britton's titration curve (*loc. cit.*) was also similar though he obtained a much less basic precipitate $Zr(OH)_{3\cdot5}\ Cl_{0\cdot5}$. That these are not equilibrium values is shown by the equilibrium titration curve shown in the same figure. In this case, the inflection occurred when 0.99 c.c. of alkali had been added, the composition of the precipitate corresponding to the formula, $Zr(OH)_{3\cdot92}\ Cl_{0\cdot08}$. This shows that even

an interval of five minutes, allowed after addition of each portion of alkali in our continued titrations, was not enough though nearly so to bring about an equilibrium.

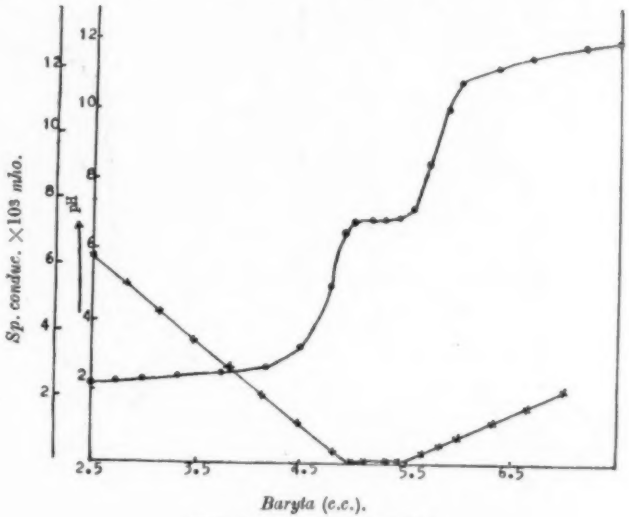


FIG. 5. Titrations of $Zr(SO_4)_2$.

Conductometric titration curves of zirconium oxychloride (Fig. 6.) against NaOH show that conductance initially falls due to the neutralisation of highly conducting hydrogen ions. Commencement of precipitation is shown by breaks in the curves in both continued and equilibrium titrations when about 0.4 c.c. of alkali has been added. The straight curves are followed by curved portions in both cases, resulting from the attack of the precipitate by the alkali. The next portion of the curve in both cases is a straight line denoting sharp rise in conductance produced by the free alkali. The amounts of alkali needed for complete precipitation in both cases, as determined by extrapolation from the curves, were practically the same as deduced from the corresponding *p*H titration curves.

Zirconium Nitrate

0.01*M* Aqueous solutions of zirconium nitrate (L. R., B.D.H) and 0.339*N* carbonate-free sodium hydroxide were used in the investigations. The purity of the sample of zirconium nitrate was checked gravimetrically.

Continued *p*H-metric and conductometric titrations show that the composition of the basic salt precipitated is $Zr(OH)_{3\cdot87}(NO_3)_{0\cdot13}$. The general appearance of the curves (Fig. 7) is similar to those in the equilibrium titration curves. These were also plotted as in the case of the oxychloride. The curves show that after three days, a more basic precipitate having the composition $Zr(OH)_{3\cdot94}(NO_3)_{0\cdot06}$ is formed.

Comparison of the results of titrations of solutions of zirconium sulphate, oxychloride and nitrate shows that the basic salts of the formulas $Zr(OH)_{3\cdot72}(SO_4)_{0\cdot14}$, $Zr(OH)_{3\cdot92}Cl_{0\cdot08}$, and $Zr(OH)_{3\cdot94}(NO_3)_{0\cdot06}$ are obtained at equilibrium with excess of sodium hy-

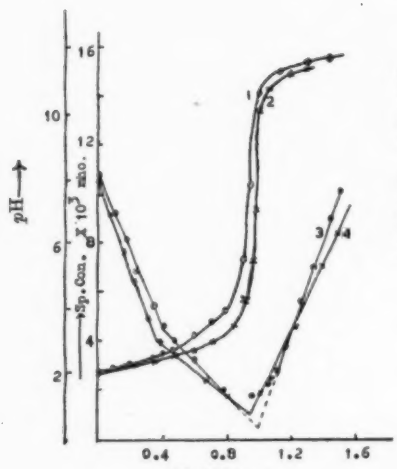


FIG. 6. Titrations with $ZrOCl_2$.
1, 4 : Contd. titrations.
2, 3 : Bottle ,,

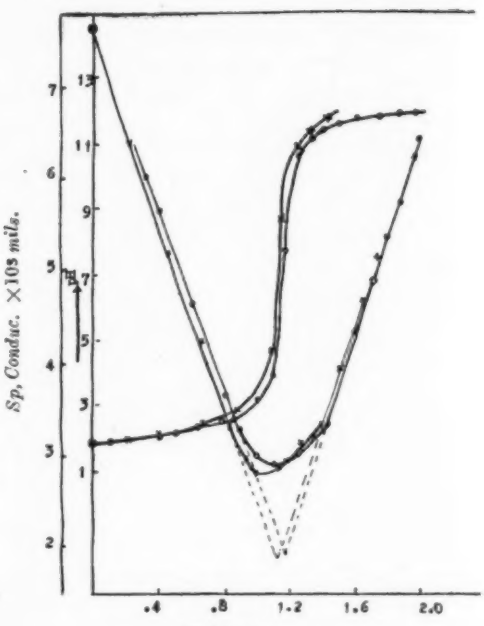


FIG. 7. Titrations with $Zr(NO_3)_4$
×—Contd. titrations.
o—Bottle ,,

droxide. Thus anion penetration is greatest in the case of sulphate and is the least in the case of nitrate. This is in conformity with the fact that the order of co-ordinating power of these ions is also the same (Bailar, "The Chemistry of Co-ordination Compounds", Reinhold Publishing Corporation, 1956, p.446).

CHEMISTRY DEPARTMENT,
UNIVERSITY OF DELHI,
DELHI-6.

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Synthetic Gonadogens. Part III. Synthesis of 4-(2′-Methyl-5′-ketocyclohexyl)-2-(4″-ketocyclohex-2″-enyl)-butane[n]

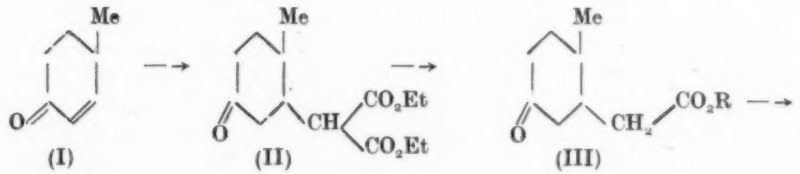
V. S. Gaind*, S. P. Narula, C. Swaroop, and S. M. Mukherji**

Synthesis of the compound, named in the title, has been achieved through the use of the Birch-Wilds method of reduction.

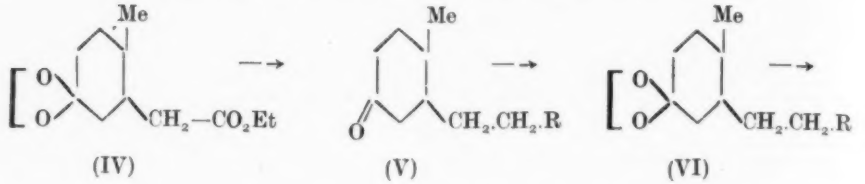
In continuation of our previous work (this *Journal*, 1956, **33**, 765) we have carried out the synthesis of 4-(2′-methyl-5′-ketocyclohexyl)-2-(4″-ketocyclohex-2″-enyl)-butane[n] (X). This structure is considered to be the ring B-C open analogue of physiologically active D-homosteroid androgens (Shoppee, "Chemistry of Steroids", Butterworth Scientific Publications, 1958, p. 155). The report by Blanchard *et al.* (*Endrocrin.*, 1943, **32**, 307; *J. Amer. Chem. Soc.*, 1943, **65**, 1579) on the estrogenic activity of 1-(*m*-hydroxyphenyl)-3-(*p*-hydroxyphenyl)-hexane, coupled with the transformation of 19-nortestosterone on aromatisation of ring A into the estrogen, estrone, and further, the observation that the absence of Δ^4-unsaturation as in dihydrotestosterone and 17-α-methyldihydrotestosterone (Rubin *et al.*, *J. Org. Chem.*, 1950, **15**, 292) does not diminish the androgenic activity, suggest the desirability of synthesising hydroaromatic structures of type (X).

The starting material, 4-methylcyclohex-2-enone (I), was obtained essentially according to Wilds and Nelson (*J. Amer. Chem. Soc.*, 1953, **75**, 5360).

The reaction sequence employed is illustrated as follows :

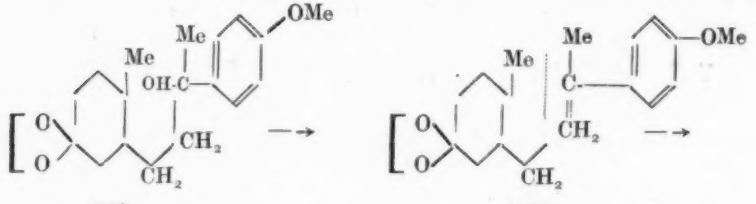


*Present address: Punjab Engineering College, Chandigarh.
**Present address: University College, Kurukshetra, Punjab.

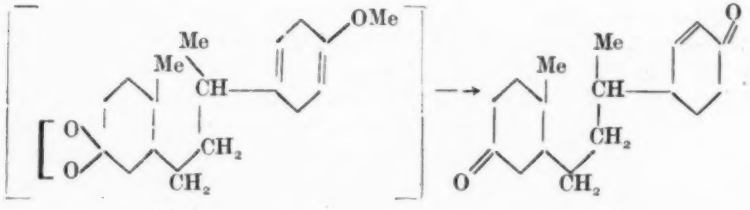


(IV) (V) (VI)

{a: R=OH. b: R=Br.} {a: R=Br. b: R=CN. c: R=CO_2K. d: R=COCl. e: R=COMe.}



(VII) (VIII)



(IX) (X)

The ketone (I) on being subjected to the Michael condensation with diethyl malonate in presence of traces of sodium ethoxide gave diethyl (3-oxo-6-methylcyclohexyl)-malonate (II) (55.5%), which on hydrolysis and decarboxylation furnished (3-oxo-6-methylcyclohexyl)-acetic acid (IIIa) in 50% yield; (IIIa) on estrification under a Dean and Stark apparatus afforded (IIIb) in 75% yield. The ketone-ester (IIIb) was then ketalised with ethylene glycol in benzene in presence of catalytic amount of P. T. S. to obtain ethyl [3-oxo-(3-dioxolane)-6-methylcyclohexyl]-acetate (IV) in 84% yield.

The ester (IV) on subsequent reduction with $LiAlH_4$ furnished β-(3-oxo-6-methylcyclohexyl)-ethyl alcohol (Va) in 75% yield, which was converted to the bromide (Vb) with PBr_3 in anhydrous benzene in 80% yield. (Vb) was ketalised as earlier to obtain β-[3-oxo-(3-dioxolane)-6-methylcyclohexyl]-ethyl bromide (VIa) in 81% yield.

The ketal-bromide (VIa) was refluxed with a water-ethanol mixture of potassium cyanide for 24 hours to obtain β-3-[oxo-(3-dioxolane)-6-methylcyclohexyl]-ethyl cyanide (VIb) in 81.8% yield. The nitrile was then allowed to react with methyl-magnesium iodide in anhydrous benzene to obtain β-[3-oxo-(3-dioxolane)-6-methylcyclo-

hexyl]-ethyl methyl ketone (VIe) in 37% yield. By this method it was difficult to obtain the pure ketone because of the proximity of the boiling points of the nitrile and the ketone.

Alternatively, for obtaining the pure ketone (VIe), potassium β-[2-methyl-5-keto-(5-dioxolane)-cyclohexyl]-propionate (VIc) was prepared by hydrolysis of the nitrile(VIb) with 20% EtOH-KOH in 68.4% yield. The potassium salt (VIc) was converted into the acid chloride (VId) by the action of oxalyl chloride in benzene (cf. Adams and Ulich, *J. Amer. Chem. Soc.*, 1920, **42**, 605); yield was not recorded because the chloride tended to decompose on distillation. The crude compound (VId) was subsequently treated with cadmium-dimethyl in benzene at the reflux temperature according to the method of Cason and Prout (*ibid.*, 1944, **66**, 46) to obtain (VIe) in 73.1% yield.

The ketal-ketone (VIe) was subsequently allowed to react with *p*-anisylmagnesium bromide in anhydrous sulphur-free benzene to obtain the intermediate carbinol (VII) (not isolated), which on distillation in presence of an iodine crystal furnished 4-[2′-methyl-5′-keto-(5′-dioxolane)-cyclohexyl]-2-*p*-anisyl-2-butene (VIII) in 45% yield. The olefine (VIII) was subjected to lithium-alcohol-anhydrous ammonia reduction and the hydro derivative (IX) was hydrolysed and isomerised with 5% hydrochloric acid (cf. Wilds and Nelson, *loc. cit.*) to obtain 4-(2′-methyl-5′-ketocyclohexyl)-2-(4″-ketocyclohex-2″-enyl)-butane[n] (X) as a pallid viscous liquid in 45% yield.

*EXPERIMENTAL

(*a*). *Diethyl (3-Oxo-6-methylcyclohexyl)-malonate* (II).—To sodium ethoxide (from 1.5 g. of sodium) was introduced, in the cold and to the exclusion of moisture, freshly distilled diethyl malonate (32g.) 4-Methylcyclohex-2-enone (22 g.), dissolved in minimum quantity of anhydrous ether, was added dropwise with vigorous shaking in ½ hour. The reaction mixture was kept at about 0° for 50 hours and then acidified with glacial acetic acid. The organic layer was extracted with ether; the ethereal extract was washed once with water, twice with dilute sodium carbonate solution, and again with water until washings were neutral to litmus. After drying (anhyd. Na_2SO_4) and removal of the ether, the residue was distilled in *vacuo* to obtain a yellowish mobile liquid, b.p. 167°/6 mm, yield 55.5%. (Found: C, 62.27; H, 8.11. $C_{14}H_{22}O_5$ requires C, 62.2; H, 8.2%).

The *semicarbazone* of (II), prepared by the usual procedure, was crystallised from ethanol, m.p. 154°. (Found: N, 12.79. $C_{15}H_{25}O_5N_3$ requires N, 12.84%).

(*b*). Potassium butoxide[t] (7.8 g.) was cooled to 0° and diethyl malonate (32 g.) was added dropwise with shaking. 4-Methylcyclohex-2-enone (22 g.) was introduced gradually with shaking. The reaction mixture after having been kept at room temperature for about 20 hours was acidified with glacial acetic acid. After working up as in (*a*), ester (II) was obtained as a pallid oil, yield 4 g.

3-*Oxo*-6-*methylcyclohexylacetic Acid* (IIIa).—A mixture of the preceding ester (20 g.), HCl (40 c.c., *d* 1.19), and water (160 c.c.) was refluxed for 10 hrs. After removal of HCl under reduced pressure, water (50 c.c.) was added to the residue; the organic material was

*M. p.'s and b.p.'s uncorrected. Microanalyses by Drs. Weiler and Straus, Oxford.

taken up in ether and dried (anhyd. Na_2SO_4). On removal of the solvent, the residual oil was distilled under reduced pressure, yield 10 g. (50%), b.p. 164-66°/6mm. (Found: C, 63.20; H, 21. $C_9H_{14}O_3$ requires C, 63.51; H, 8.29%).

Ethyl (3-*Oxo*-6-*methylcyclohexyl*)-*acetate* (IIIb).—A mixture of the acid (IIIa) (20 g.), absolute ethanol (8 g.), anhydrous benzene (100 c.c.), and H_2SO_4 (conc., 1 c.c.) was refluxed in a Dean and Stark apparatus till no more water had separated. The mixture was cooled and the organic material was taken up in ether-benzene. After working up in the usual manner, the ester (IIIb) was obtained as a yellow oil, b.p. 129-30°/8mm, yield 20 g. (Found: C, 66.22; H, 9.23. $C_{11}H_{18}O_3$ requires C, 66.64; H, 9.15%).

Its *semicarbazone* was crystallised from ethanol, m.p. 145°. (Found: N, 16.43. $C_{12}H_{21}O_3N_3$ requires N, 16.46%).

Its 2,4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method as deep orange needles (ethanol), m.p. 138°. (Found: N, 14.56. $C_{17}H_{22}O_6N_4$ requires N, 14.81%).

Ethyl [3-*Oxo*-(3-*dioxolane*)-6-*methylcyclohexyl*]-*acetate* (IV).—A mixture of the ester (IIIb) (20 g.), ethylene glycol (7 g.), anhydrous benzene (200 c.c.), and P.T.S. (0.2 g.) was refluxed under a constant water separator (Dean and Stark type) until no more water had collected (8 hrs.). The reaction mixture was cooled, the excess of P.T.S. was destroyed with a little sodium ethoxide in ethanol, and sufficient amount of water was added. The organic phase was separated and the aqueous layer was extracted with ether. The combined extract was washed with water and dried (anhyd. Na_2SO_4). Distillation of the product under reduced pressure, after removal of the solvent, furnished 20 g. (84%) of a yellow oil boiling at 135°/5mm. (Found: C, 64.6; H, 9.02. $C_{13}H_{22}O_4$ requires C, 64.44; H, 9.15%).

β-(3-*Oxo*-6-*methylcyclohexyl*)-*ethyl Alcohol* (Va).—A slurry of $LiAlH_4$ (1.4 g.) in anhydrous ether (100 c.c.) was placed in a 500 c.c. three-necked flask, equipped with a glycerol-sealed mechanical stirrer, an addition funnel, and a reflux condenser fitted with $CaCl_2$ drying tube. A solution of the ester (IV) (16 g.) in dry ether was added with efficient stirring to maintain the ether at gentle reflux. The contents were then refluxed for 1 hour, cooled, treated with water (10 c.c.), and then with 20% H_2SO_4 (100 c.c.). The organic material was taken up in ether. The ethereal solution was washed successively with water, $NaHCO_3$ solution, and water and dried (anhyd. Na_2SO_4). After removing the solvent, the residue was distilled under reduced pressure to obtain a light, colorless oil, b. p. 120°/12 mm, yield 12 g. (75%). (Found: C, 69.17; H, 10.13. $C_9H_{16}O_2$ requires C, 69.19; H, 10.32%).

β-(3-*Oxo*-6-*methylcyclohexyl*)-*ethyl Bromide* (Vb).—To a cooled solution of (Va) (20 g.) in anhydrous benzene (20 c.c.) with three drops of dry pyridine was added phosphorus tribromide (15 g.) during 5 mins. The mixture was allowed to attain room temperature and kept there for another 1½ hrs. It was finally heated at 60-65° for about 1 hour, cooled, and then poured into ice-water. The organic substance was extracted with ether. The ethereal extract was washed successively with water, cold dilute $NaHCO_3$ solution (5%), and water and dried. On removal of the solvent the residue was fractionated from a Claisen head, when the bromide (Vb) was obtained as a yellow mobile liquid, b.p. 137-40°/7 mm, yield 28.8 g. (80%). (Found: C, 49.03; H, 6.82; Br, 36.33. $C_9H_{15}OBr$ requires C, 49.31; H, 6.84; Br, 36.53%).

β-[3-*Oxo*-(3-*dioxolane*)-6-*methylcyclohexyl*]-*ethyl Bromide* (VIa).—A mixture of the compound (Vb) (20 g.), ethylene glycol (7 g.), anhydrous benzene (200 c.c.), and P.T.S. (0.2 g.) was treated as before to obtain the ketal bromide (VIa) as an oil, b.p. 138-40°/6mm, yield 20 g. (84%). (Found: C, 50.17; H, 7.29; Br, 30.11. $C_{11}H_{19}O_2Br$ requires C,50.19; H, 7.22; Br, 30.41%).

β-[3-*Oxo*-(3-*dioxolane*)-6-*methylcyclohexyl*]-*ethyl Cyanide* (VIb).—To a solution of potassium cyanide (4.6 g.) in water (10 c.c.) was added gradually, with stirring and to the exclusion of moisture, the preceding bromide (VIa) (15 g.) mixed in 95% ethanol (20 c.c.) during ½ hr. The mixture was refluxed for 24 hours, filtered under suction, and the residue was washed with ethanol (10c.c.×2). Most of the solvent was distilled. The residual mixture was then poured into ice-water and the organic material was extracted with ether. From the ethereal solution after removal of the solvent, compound (VIb) was obtained in 9 g. yield(81.8%), b.p. 120°/7 mm. (Found: C, 68.72; H, 9.14; N, 6.63. $C_{12}H_{19}O_2N$ requires C, 68.86; H, 9.15; N, 6.69%).

β-[3-*Oxo*-(3-*dioxolane*)-6-*methylcyclohexyl*]-*ethylmethyl Ketone* (VIe).—A solution of methylmagnesium iodide was prepared from dry magnesium turnings (1.2 g.), methyl iodide (7 g.), and anhydrous ether (30c.c.). To this was added, under cooling, the compound (VIb) (10 g.), dissolved in dry ether (10 c.c.). Most of the ether was replaced by dry sulphur-free benzene (40 c.c.). The contents were refluxed for 6 hours on a steam bath. The Grignard complex was hydrolysed with aqueous ammonium chloride; the benzene layer was separated and the aqueous phase was extracted thoroughly with ether. The combined extract was washed with water repeatedly and dried (Na_2SO_4). The solvent was removed and the residue was distilled in vacuum to obtain 4 g. (37%) of the ketone (VIe) as a mobile colorless oil. (Found: C, 69.11; H, 7.78. $C_{13}H_{22}O_3$ requires C, 68.99; H, 9.8%).

The *bis*-2,4-*dinitrophenylhydrozone* of (VIe) was crystallised from ethyl acetate-ethanol mixture, m.p. 148°. (Found: N, 19.23. $C_{25}H_{30}O_9N_8$ requires N, 19.11%).

β-[2-*Methyl*-5-*keto*-(5-*dioxolane*)*cyclohexyl*]-*propionyl Chloride* (VId).—A mixture of the above cyanide (VIb) (30 g.) and 20% ethanolic KOH (100 c.c.) was refluxed for 25-30 hours until the evolution of ammonia stopped. Ethanol and water were evaporated. Last traces of water were removed in a vacuum desiccator. The residual solid K salt (VIc) weighed 26 g. (68.4%).

To a solution of oxalyl chloride (17.7 g.) in dry benzene (35 c.c.) was dropped the above potassium salt (VIc) (26 g.) in small portions so as to keep the evolution of gases under control. The mixture was then refluxed for 2 hours and the solid matter was filtered. The acid chloride (a test portion) tended to decompose during vacuum distillation. The crude material weighed 22.4 g. (93%).

β-[3-*Oxo*-(3-*dioxolane*)-6-*methylcyclohexyl*]-*ethylmethyl Ketone* (VIe).—To methylmagnesium iodide, prepared from clean dry Mg turnings (2.6 g.), MeI (15.4 g.), and dry ether (60 c.c.), was introduced anhydrous cadmium chloride (8.7 g.) in small lots under cooling and stirring. The mixture was then refluxed with stirring for 3 to 4 hrs. Ether was completely replaced by benzene (150 c.c.) and the solution heated to boiling. The acid chloride (VId) (22.4 g.) was then added with stirring at a rate so as to maintain the benzene at gentle reflux. The contents were then refluxed, stirred for about 1 hour, and cooled, when a hard solid was deposited. The mixture was then decomposed with ice-cold water.

The organic material was taken up in ether-benzene; the organic phase after drying and removing the solvent furnished (VIe) as a light mobile oil, b.p. 137°/7mm, yield 15 g. (73%). (Found: C, 69.11; H, 9.78. $C_{13}H_{22}O_3$ requires C, 68.99; H, 9.8%).

The *bis*-2,4-*dinitrophenylhydrazone* melted at 148°; mixed m.p. with sample derived from the ketal-ketone (VIb), 148°.

4-[2′-*Methyl*-5′-*keto*-(5′-*dioxolane*)-*cyclohexyl*]-2-p-*anisyl*-2-*butene* (VIII).—To the Grignard reagent, prepared from Mg (2 g.) and *p*-bromoanisole (15 g.) in dry ether (100 c.c.), wos added the preceding ketone (VIe) (15 g.) slowly under ice-cooling. The contents were allowed to stand overnight at room temperature and then refluxed for 1 hour. The reaction mixture was decomposed with a saturated solution of ammonium chloride. The oily product was extracted with ether. After drying and removal of the solvent, the residual material was distilled in presence of a crystal of iodine to obtain (VIII) as a yellowish oil, b.p. 160°/6 mm, yield 10.58 g. (50%).

4-(2′-*Methyl*-5′-*ketocyclohexyl*)-2-(4″-*ketocyclohex*-2″-*enyl*)-*butane* (X).—A solution of the olefine (VIII) (9.9 g.) in anhydrous ether (20 c.c.) was placed in a 500 c.c. three-necked flask fitted with a glycerol-sealed mechanical stirrer, a soda-lime drying tube, and an addition funnel. Liquid ammonia (150 c.c.) was run into the flask and the stirring commenced. Freshly cut lithium metal (1.75 g.) was added gradually with stirring during 15 mins. Stirring was continued for 10 mins. more and anhydrous ethanol (13.0 g.) was added dropwise in 15 mins., when the blue colour was discharged. The ammonia was then removed, water and ether were added, and the mixture was left for ½ hr. The organic material was extracted with ether. Removal of the ether left the dihydro derivative (IX) as an oily liquid, which was hydrolysed with 5% EtOH-HCl (40 c.c.) at water bath temperature for 2 hrs. Ethanol was then removed and the residual mixture was extracted with ether. The ethereal layer was washed free of acid, dried, the solvent removed, and vacuum distilled to afford a yellowish viscous oil, b.p. 158°/6mm, yield 3.6 g. (45%).

The compound (X) gave a *bis*-2,4-*dinitrophenylhdrozone* which was crystallised from ethyl acetate-ethanol in orange red needles, m.p. 151°. (Found: N, 18.01. C_{29}-$H_{34}O_9N_8$ requires N, 18.01%).

Department of Chemistry,
Punjab University,
Chandigarh.

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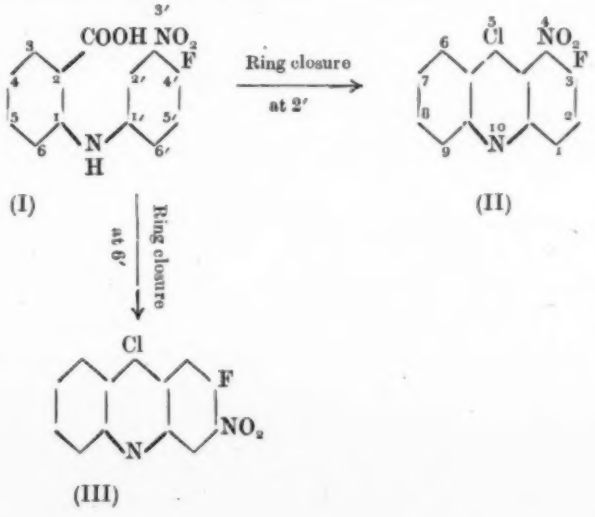
Organic Pesticides. Part VII. Synthesis of certain Fluoro-acridines

K. C. Joshi and S. C. Bahel

3-Fluoro-5-chloro-7-bromoacridine, 3,7-difluoro-5-chloroacridine and its 5-substituted derivatives, the isomers 3-fluoro-4-nitro-5-chloroacridine and 2-nitro-3-fluoro-5-chloroacridine, and their 5-substituted derivatives have been synthesised as potential pest-control chemicals.

Usually, an unsubstituted nucleus containing heterocyclic nitrogen is seldom fungitoxic. Acridine is, however, known to be toxic to spores of various rusts (Straib, *Zentral. Bakt. Abs.* 2., 1941, **103,** 73). Horsfall and Rich (Contributions from Boyce Thomson Institute, 1951, **16,** 316) evaluated a large number of heterocyclic nitrogen compounds by the spore-germination technique against *Sclerotinia fructicola* and *Macrosporium sarcinaeforme* and found acridine to be fairly active. The only work done so far on fluoro-acridines is by Wilkinson and Finar (*J. Chem., Soc.*, 1947, 759). We have therefore attempted to synthesise acridines containing fluorine, either in the nucleus or in addition in an aromatic side chain at position 5.

4-Fluoro-3-nitroaniline was condensed with *o*-chlorobenzoic acid to obtain 4′-fluoro-3′-nitrodiphenylamine-2-carboxylic acid (I) having a substituent in position 3′, which on cyclisation with phosphorus oxychloride gave two isomeric acridines depending on whether the ring closure occurred at 2′- or 6′-position. These were separated from toluene by fractional crystallisation (vide Experimental).



We have not been able to synthesise by an additional independent method either of these isomers so far and the structures assigned to them are based on observations made earlier by various workers in similar other cases (Lehmstedt and Schrader, *Ber.*, 1937, **70,** 838; Albert and Linnell, *J. Chem. Soc.*, 1942, 377; Bradburry and Linnell, *ibid.*, 1942, 377). In all these cases a negative substituent in 3′-position is reported to provide a ratio of *ortho* to *para* closure as 75:25, whereas a positive substituent, about 20:80. Keeping in view these generalisations and our own observations, we have provisionally suggested the structures (II, yield 67%) and (III, yield 33%). The other fluoro-acridines were prepared by the usual method.

EXPERIMENTAL

4′-Fluoro-3′-nitrodiphenylamine-2-carboxylic Acid (I) was obtained by refluxing *o*-chlorobenzoic acid (45 g.), anhydrous potassium carbonate (45 g.), 4-fluoro-3-nitroaniline (56 g.), amyl alcohol (150 c.c.), and freshly prepared dry copper powder (3g.) at 140° for 5 hours. The resulting solution was steam distilled, diluted with water, boiled with animal charcoal, and filtered. The filtrate on acidification gave a solid which crystallised from glacial acetic acid, m.p. 175°, yield 45 g. (46%). (Found: N, 10.02. $C_{13}H_9O_4N_2F$ requires N,10.14%).

Formation of 3-Fluoro-4-nitro-5-chloroacridine (II) *and 3-Fluoro-2-nitro-5-chloroacridine* (III).—The compound (I) (45 g.) and $POCl_3$ (150 c.c.) were heated on a steam bath for 15 minutes and then in an oil bath at 120° for 4 hours. Excess of $POCl_3$ was removed under reduced pressure at a bath temperature of 140° and the resulting liquid was poured into a well-stirred, cold solution of ammonia and chloroform. The chloroform layer was separated, washed with water, dried, chloroform evaporated, and the solid obtained was dried in *vacuo*; yield 30 g., m.p. 120°.

The product was gently refluxed with toluene for a few minutes and filtered hot. The undissolved residue was repeatedly extracted with boiling toluene, filtered, and finally washed with cold toluene. This insoluble product was assigned the structure (III), yield 10 g., m.p. 265° (decomp.). (Found: N,9.92. $C_{13}H_6O_2N_2ClF$ requires N,10.12%). The residue obtained on evaporation of the mother liquor weighed 20 g., m. p. 155° (decomp.) and was assigned the structure (II). (Found: N, 9.96. $C_{13}H_6O_2N_2ClF$ requires N, 10.12%).

Formation of 3-Fluoro-4-nitro-5-phenoxyacridine was effected by heating 3-fluoro-4-nitro-5-chloroacridine (2 g.) with phenol (10 g.) at 120° for 3 hours and then pouring the mixture into 2*N*-NaOH (60 c.c.). It was filtered, the yellow product obtained was washed with ether, and finally crystallised from acetic acid, m.p. 135°, yield 1.7 g. (70.8%). (Found: N 8.26. $C_{19}H_{11}O_3N_2F$ requires N, 8.38%).

3-Fluoro-4-nitro-5-phenylaminoacridine—3-Fluoro-4-nitro-5-chloroacridine (3 g.), aniline (1.5 g.), and phenol (15 g.) were heated on a steam bath for 4 hours. The mixture was cooled, triturated with ether, and filtered. The residue was washed several times with ether, dried, and dissolved in acetic acid; the solution was decomposed with ammonia and filtered. A scarlet-red product was recrystallised from aqueous ethanol, m.p. 125°, yield 1 g. (27.7%). (Found: N, 12.54. $C_{19}H_{12}O_2N_3F$ requires N 12.61%).

3-*Fluoro*-2-*nitro*-5-*phenoxyacridine* was obtained from 3-fluoro-2-nitro-5-chloroacridine (2 g.) and phenol (10 g.) by following the above procedure. The product was dull yellow in colour, m.p. 245°, yield 2 g. (83.3%). (Found: N, 8.22. $C_{19}H_{11}O_3N_2F$ requires N, 8.38%).

3-*Fluoro*-2-*nitro*-5-*phenylamincacridine* was prepared from 3-fluoro-2-nitro-5-chloroacridine (3 g.), aniline (1.5 g.), and phenol (15 g.) by following the above procedure. A dull red product was obtained; m.p. 250°, yield 1.2 g. (33.2%). (Found: N, 12.48. $C_{19}H_{12}O_2N_3F$ requires N, 12.61%).

4,4′-*Difluorodiphenylamine*-2-*carboxylic acid* (IV) was obtained by refluxing a mixture of 3-fluoro-6-bromobenzoic acid (21 g.), anhydrous potassium carbonate (14 g.), *p*-fluoroaniline (16 g.), amyli-alcohol (60 c.c.), and a trace of freshly prepared dry copper powder according to the procedure given earlier. The compound is light grey in colour, m.p. 220° (decomp.), yield 16.5 g. (69.3%). (Found: N, 5.51. $C_{13}H_9O_2NF_2$ requires N, 5.62%).

Formation of 3,7-*Difluoro*-5-*chloroacridine*.—The compound (IV) (16.5 g.) was cyclised by means of $POCl_3$ (55 c.c.) according to the procedure mentioned earlier, yielding 3,7-difluoro-5-chloroacridine. The product is yellowish green in colour, m.p. 169°, yield 15 g. (90%). (Found: N, 5.51. $C_{13}H_6NClF_2$ requires N, 5.61%).

3,7-*Difluoro*-5-*phenoxyacridine* was obtained from the above compound (2 g.) and phenol (10 g.) by the usual procedure and crystallised from aqueous ethanol, m.p. 161° (decomp.), yield 2.0 g. (83.3%). (Found : N, 4.42. $C_{19}H_{11}ONF_2$ requires N, 4.56%).

3,7-*Difluoro*-5-*phenylaminoacridine*.—The above compound (5 g.), aniline (2 g.), and phenol (30 g.) were heated on a steam bath for 4 hours. The mixture was triturated with ether when the hydrochloride separated. It was filtered and washed well with ether, m.p. 335°, yield 5 g. (73.5%). (Found: N, 8.07. $C_{19}H_{13}N_2ClF_2$ requires N, 8.17%).

The *hydrochloride* was dissolved in acetic acid and the free base was liberated by decomposing the acetic acid solution in cold with ammonia, m.p. 193°, yield 3.5 g. (57.3%). (Found: N, 9.02. $C_{19}H_{12}N_2F_2$ requires N, 9.14%).

3,7-*Difluoro*-5-p-*fluorophenylaminoacridine* was obtained from the previous compound (2.5 g.), *p*-fluoroaniline (1.5 g.), and phenol (15 g.) by the above procedure. Yield of the *hydrochloride* was 3 g. (83.3%), m.p. 350°. (Found: N, 7.64. $C_{19}H_{12}N_2ClF_3$ requires N, 7.73%). Yield of the *free base* was 2 g. (62.5%), m.p. 198°. (Found: N, 8.48. $C_{19}H_{11}N_2F_3$ requires N, 8.64%).

3,7-*Difluoro*-5-α-*naphthylaminoacridine* was obtained from the previous compound (3 g.), α-naphthylamine (3 g.), and phenol (20 g.) by following the above procedure. Yield of the *hydrochloride* was 3 g. (50.8%), m.p. 172°. (Found: N, 6.89. $C_{23}H_{15}N_2ClF_2$ requires N, 7.13%). Yield of the *free base* was 2 g. (46.7%) m.p. 73°. (Found: N, 7.64. $C_{23}H_{14}N_2F_2$ requires N, 7.86%).

4′-*Fluoro*-4-*bromodiphenylamine*-2-*carboxylic acid* was obtained by refluxing 2-chloro-5-bromobenzoic acid (prepared by the method of Cohen and Smithells, *J. Chem. Soc.*, 1914, **105**, 1911) (1.5 g.), anhydrous potassium carbonate (2 g.), *p*-fluoroaniline (2 g.),

amyl alcohol (5 c.c.), and a trace of freshly prepared dry copper powder; m.p. 190° (decomp.), yield 1.5 g. (76%). (Found: N 4.32. $C_{13}H_9O_2NBrF$ requires N, 4.50%).

Formation of 3-*Fluoro*-7-*bromo*-5-*chloroacridine*.—The above compound (1.5 g.) and $POCl_3$ (5 c.c.) by the usual procedure afforded 3-fluoro-7-bromo-5-chloroacridine, m.p. 135°, yield 1 g. (66%). (Found : N, 4.38. $C_{13}H_6NBrClF$ requires N, 4.50%).

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CHEMICAL LABORATORIES,
UNIVERSITY OF GORAKHPUR,
GORAKHPUR, U.P.

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Electrochemical Studies on Lead Electrode

S. A. Awad and T. M. Salem

An electrochemical study on the behaviour of freshly electroplated and aged lead electrodes in solutions of varying *p*H, initially free from lead ions, has been made; the probable existence of an oxide film on the surface of metals has also been discussed.

Behaviour of these electrodes has been examined in universal buffer mixtures at different temperatures. By comparing the results obtained, the behaviour in alkaline range is found to be governed by PbO, but in the acid range it is governed by a persistent phosphate film in phosphate buffers or an oxide in acetate buffers.

Although the lead electrode (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Longmans, Green and Co., London, Vol. 7, 1947, p. 649; Nayer and Pande, *Proc. Ind. Acad. Sci.*, 1948, **27A**, 343; Compton and Mendizza, *Corrosion*, 1949, **5**, 194; Rell, *ibid*, p. 261; ElWakked and Salem, Electrochem. Soc. Meeting, Cincinnati, Ohio, 1955, No. 60; Ito and Shibane, *Chem. Abs.*, 1957, **51**, 6308) has been extensively investigated, no systematic study of its behaviour in solutions of varying *p*H is available. The present investigation throws light on its behaviour in solutions of different *p*H in presence of air.

EXPERIMENTAL

The electroplated lead electrode used was prepared after Mathio (*Zhur. Priklad Khim.*, 1956, **28**, 236) from 0.8-1.0*N* solutions of lead plumbite using a current of 10 m.a./cm^2 of a platinum plate electrode for 30 minutes. The anode was a rod of pure lead provided by Sherring Kahlbaum Company.

Buffer solutions of varying *p*H (2.98 to 10.97) were prepared according to Smith ("Analytical Processes. A Physico-Chemical Interpretation", 1949, p.442). Another series of buffer solutions covering the *p*H range 1.7 to 11.88 was also prepared (Britton, "Hydrogen Ions", Vol. I, 1955, p. 365, Chapman and Hall). For the extreme acid and alkaline ranges, nitric acid and sodium hydroxide solutions were used. The *p*H values of these solutions were checked with the hydrogen electrode and, when possible, with the quinhydrone electrode. All buffer solutions were used undiluted.

The behaviour of the lead electrode as an indicator electrode was examined in the titration of the universal buffer mixtures with 0.2*M*-NaOH solutions at different temperatures, ranging from 25° to 50°. For this purpose a water thermostat was used where temperature was kept constant within a range of $\pm 0.05°$.

Electrical Measurements.—The measurements were carried out in duplicate with different stock solutions. The potential of the lead electrode was measured by coupling it with a saturated calomel electrode as half cell, of which the potential value amounted to 0.245 volt at 25°. Measurements were made with a Cambridge potentiometer.

DISCUSSION

Fig. 1 shows that with the electroplated lead electrode, slopes obtained from *p*H 1.0 to 8.0 deviate from the theoretical for the hydrogen electrode. The potentials from *p*H 8.0 to 12.6 are linear function of the *p*H of the solution. At the extreme alkaline ranges, the electrode shows an irregular variation in potential. The E^{o}_{H} value for the range (8 to 12.6) was found to be + 0.250 volt.

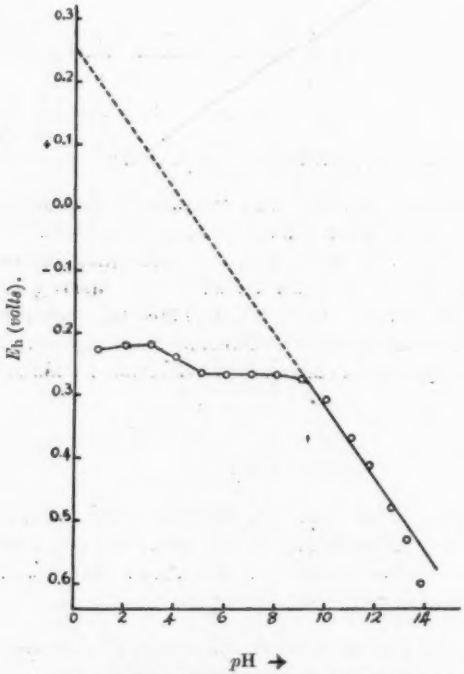

FIG. 1. Electroplated lead electrode in acetate buffer solution of varying *p*H in air.

Fig. 2 (A and B) shows the potential—*p*H curves obtained in phosphate buffer solutions after 4 and 24 hours. The potential values obtained in acid regions A_1 and B_1 deviate from the hydrogen electrode, $\triangle E/\triangle p$H is 32mv. In curves A_2 and B_2 the potential is linear giving the E^{o}_{H} values as + 0.188v and + 0.248v respectively. The potential value obtained at *p*H 11.3 and 11.8 are much lower than expected values.

In aqueous solutions, oxide film formation in air is usually attributed to the transfer

of electrons to dissolved oxygen, transforming it into OH^- ions which are attracted to the metal lattice, forming an oxide film (ElWakked and Salem, *loc. cit.*).

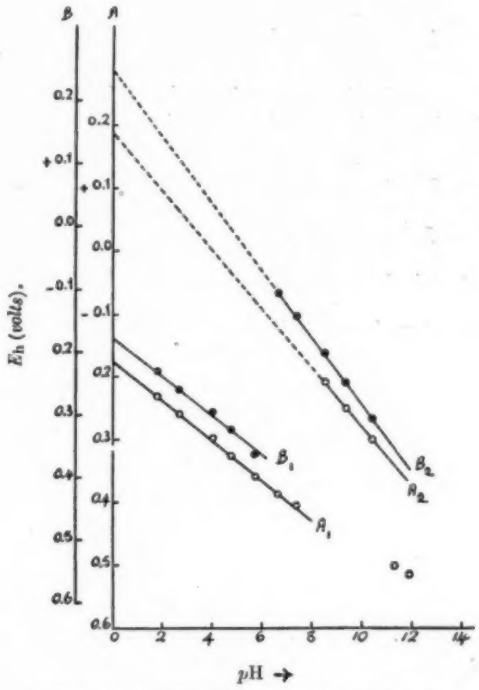

FIG. 2.(A) Equilibrium values of lead electrode in universal phosphate buffer after 4 hrs.

(B) The same after 24 hrs.

To ascertain which type of oxide is formed on the electrodeposited lead electrode in air, one can calculate the free energy change (Latimer, "Oxidation Potentials", Prentice Hall, 1953, pp.39, 152) of the reaction:

$$Pb + H_2O \longrightarrow PbO + 2H^+ + 2e$$

to be + 11440 cals. This gives $E^o{}_H$ value of 0.248 volt. This indicates that PbO is the oxide responsible for the linearity of the potential—*p*H curves in Figs. 1 and 2.

In the alkali range *p*H 12.6 to 13.8 (Fig. 1) and *p*H 11 to 12 (Fig, 2), the lead oxide formed, owing to its great solubility in such solutions, will lead to variation in the *p*H; the activity of the Pb^{++} in the solution at the interphase causing it to decrease, the potential value measured deviates from that expected. The local change of *p*H in the vicinity of the electrode was found previously for mercury, tungsten, and tin (ElWakked *et al.*, *J. Phys. Chem.*, 1952, **56**, 621; 1955, **59**, 1004; *J. Chem.Soc.*, 1957, 3770).

In the acid range of *p*H 1 to 6 (Fig. 2, A_1 and B_1) it is suggested that in this region a persisting film of lead secondary phosphate is formed on the surface of the electrodes. The results can be expressed by the equation:

$$E = E'_0 - \frac{RT}{2F} \ln [HPO_4^{2-}]$$

It can be shown theoretically that up to *p*H 6, the activity of secondary phosphate ion is inversely proportional to H^+ ion activity. That is

$$E = E''_0 + \frac{RT}{2F} \ln [H^+]$$

$$= E''_0 - 0.029\, p\text{H at } 25°.$$

This is in good agreement with the results obtained for the electrode $Pb/PbHPO_4^{2-}$.

Lead electrode was next used as an indicator electrode in titration of a universal buffer mixture against 0.2*M*-NaOH solution. A freshly electroplated and an aged lead electrodes were used; the latter was aged by leaving it in solution of *p*H 9 for 3 days to ensure complete formation of an oxide layer. Fig 3B shows the potential values for the aged electrode which vary linearly with the *p*H. The value for E^0_H for this electrode was found to be +0.252volt, indicating that the potential is governed by PbO. The fresh electrode in the universal buffer mixture titration (Fig. 3A) exhibits a slope of 32 mv per unit *p*H, showing that the potential within the *p*H range 1 to 6 is governed by the primary formation of a phosphate layer. Above *p*H 8.5, the deviation from linearity is attributed to the slow replacement of PbO.

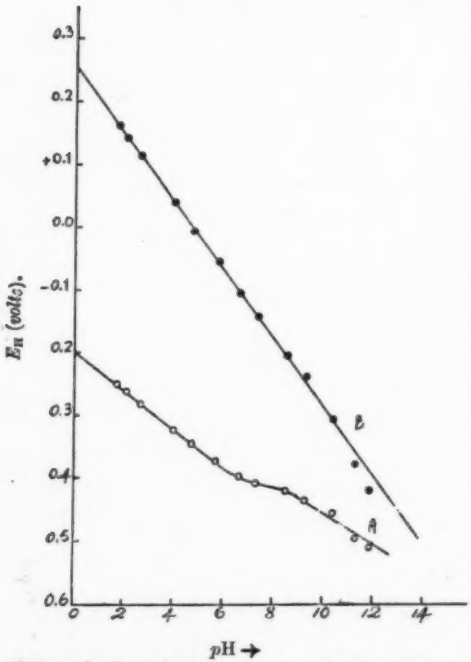

FIG. 3.(A) Fresh lead electrode in universal buffer titration.
(B) Aged lead electrode in " " "

Titration curves for the fresh electrode at temperatures higher than 35° are similar to those obtained after 24 hours in the phosphate buffers (Fig.2, B_1 and B_2) at 25°.

CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE FOR GIRLS,
AIN SHAMS UNIVERSITY,
HELIOPOLIS, CAIRO, EGYPT,
U.A.R.

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Anodic Synthesis. Part I. Ester, Ether, Primary and Secondary Alcohols

J. K. Mehrotra and A. N. Dey

An ester, an ether, three primary, and three secondary alcohols have been prepared in fair yields by anodising appropriate mixtures of acids and half esters.

Kolbe (*Annalen*, 1849, **69,** 257) showed that on electrolysis of an aqueous solution of an alkali metal carboxylate, carbon dioxide and hydrocarbon were formed.

$$2\ C_nH_{2n+1}.\ COO^- \xrightarrow{-2e} 2CO_2 + C_{2n}H_{4n+2}$$

The electrolytic syntheses have, however, been largely restricted to the electrolysis of sodium salts of saturated carboxylic acids or half esters of $\alpha\beta$-dicarboxylic acids. The yields of the coupled products obtained depend to some extent on the structure of carboxylic acids employed and on experimental conditions (Swann, *Trans. Amer. Electrochem. Soc.*, 1929, **56,** 457; Fichter *et al.*, *Helv. Chim. Acta*, 1932, **15,** 698; 1934, **17,** 1218; 1938, **21,** 141; Murray and Taylor, *J. Chem. Soc.*, 1937, 1450).

The electrolysis of a mixture of carboxylic acids (R.COOH and R′.COOH) would give rise to products both by symmetrical and unsymmetrical (crossed) couplings (R.R, R′.R′ and R.R′). The process is of wide application and affords a synthetical route to many organic compounds (Miller and Hofer, *Ber.*, 1895, **28,** 2427; Hofer, *Ber.*, 1900, **33,** 650; Carmichael, *J. Chem. Soc.*, 1922, **121,** 2545; Ruzicka *et al.*, *Helv. Chim. Acta*, 1932, **15,** 1459; Kitaura, *Bull. Inst. Phys. Chem. Res., Japan*, 1937, **16,** 765; *Chem. Abs.*, 1938, **32,** 4523; Offe, *Z. Naturforsch.*, 1947, **26,** 182; Gunstbee and Stenhagen, *Svensk Kem. Tidekr.*, 1942, **54,** 243; Hunsdiecker, *Ber.*, 1942, **75,** 447, 460, 1197; Weeden *et al.*, *J. Chem. Soc.*, 1950, 3326, 3331, 3333). The advantage of the electrolytic process lies in the easy separability of the mixture of products in high purity. It has been found by earlier workers (Brown and Walker, *Annalen*, 1893, **42,** 274; Von Miller, *Z. Elektrochem.*, 1897, **4,** 55) that even those acids, which normally produce little or no yield of the Kolbe products, when electrolysed alone, afford cross-coupled products easily with other acids in fair yields. The relative proportions of the three products are those to be expected from the composition of the initial acid mixture. A wide difference in the size and structure of the two coupling units can be tolerated; this also includes cross coupling of simple and substituted fatty acids (I) with acid half esters (II) yielding hydrocarbons (III), mono-(IV), and dicarboxylates (V)(say Me):

$$\underset{\text{(I)}}{R.COOH} + \underset{\text{(II)}}{HOOC.\ (CH_2)_n.\ COOMe} \longrightarrow \underset{\text{(III)}}{R.R};\ \underset{\text{(IV)}}{R.(CH_2)_n.COOMe};$$

$$\underset{\text{(V)}}{MeOOC.\ (CH_2)_{2n}.COOMe}$$

With a view to standardising this method for the preparation of certain other compounds, an ester, an ether, three primary, and three secondary alcohols have been prepared by cross

coupling of mixtures of acids and half esters (Table I). As only cross-coupled products were required, in some cases the other products formed during electrolysis had not been fully worked up.

TABLE I

No.	Acids and half esters.	Cross-coupled products.	Yields (calc. from the acid).
1.	Butyric acid + ethyl hydrogen succinate	Ethyl caproate[n]	32% from butyric
2.	Phenylacetic acid + phenoxy-acetic acid	β-Phenoxyethylbenzene	13.7% from phenoxyacetic
3.	Lauric acid + glycollic acid	Lauryl alcohol	27.4% from lauric
4.	Myristic acid + glycollic acid	Myristyl alcohol	24.7% from myristic
5.	Palmitic acid + glycollic acid	Cetyl alcohol	13.7% from palmitic
6.	Lauric acid + lactic acid	*dl*-Tridecanol-2	20% from lauric
7.	Myristic acid + lactic acid	*dl*-Pentadecanol-2	22.4% from myristic
8.	Palmitic acid + lactic acid	*dl*-Heptadecanol-2	13.2% from lactic

EXPERIMENTAL

The apparatus used for electrolysis consisted of a boiling tube, 2″ in diameter and 9″ in length, fitted with a thermometer, a mechanically driven glass stirrer, a spiral anode of Pt wire, 24 swg and 20 cm long (total surface area 3.51 cm^2), and a platinum plate cathode of 1.4 cm^2. The cell was clamped in a wide-mouth thermosflask, which was filled with a mixture of crushed ice and water so as to keep the cell cooled. The cell was connected in series with an ammeter, rheostat, and mains.

Ethyl Caproate.—Pure butyric acid(8.8 g., 0.1*M*) and ethyl hydrogensuccinate (14.6g., 0.1*M*) were dissolved in 50% methanol (100 c.c.). To this a solution of metallic sodium (0.46 g., 0.02 g. atom) in methanol (5.c.c.) was added. The mixture was placed in the anodising cell and a current of 2.2 amps. was passed through the cell for 3½ hours (theoretical current, 5.36 amps.) with vigorous stirring, while the cell was externally cooled by ice-water mixture to keep the internal temperature of the cell below 30°. At the end of the period the mixture became alkaline. The solvent was removed from the anodised solution at a low temperature. The distillate containing hexane[n] (lit. b.p. 68.4°) was not further worked up. The residue was dissolved in ether (50 c.c.) and the ethereal layer was washed with small instalments of 2% NaOH solutions so as to remove last traces of any free acid. It was finally washed with two 10 c.c. portions of water. The organic layer was dried over fused $CaCl_2$. Ether was removed by distillation and the residue fractionally distilled. Two portions, one boiling below 190° and the other boiling between 190° and 250°, were collected. The latter on distillation gave 4.8 g. of pure diethyl adipate, b.p. 239-42° (lit. b.p. 245°). The former fraction on redistillation gave 4.6 g. of pure ethyl caproate[n], b.p. 167-68° (lit. b.p. 166-67°); caproic acid, b.p. 205° (lit. b.p. 205°); anilide, m.p. 95°.

β-Phenoxyethylbenzene.—A mixture of a solution of phenoxyacetic acid (15.2g., 0.1*M*), phenylacetic acid (13.6g., 0.1*M*), and sodium (0.46g., 0.02g. atom) in 98% methanol (100 c.c.) was anodised by passing a current of 1.5 to 1.7 amps. for 5¼ hrs., when the solution became alkaline. The solvent was removed from the anodised solution at a

low temperature and the residue dissolved in ether. The ethereal layer was washed with 1% NaOH and dried. The solvent was again removed and the residue distilled, collecting whole of the fraction passing between 90° and 180°/10 mm. The residue (7.8 g.) containing mainly diphenyl ethyl ether was not purified further. The distillate was refractionated, collecting 6.8 g. of dibenzyl, b.p. 137-41°/10 mm (lit. b.p. 140-50°/13 mm) and 2.7 g. of β-phenoxyethylbenzene, b.p. 168-70°/15 mm (lit. b.p. 162-63°/14 mm). (Found: C, 84.85; H, 6.38. Calc. for $C_{14}H_{14}O$: C, 84.85; H, 7.07%).

Lauryl Alcohol.—A mixture of a solution of lauric acid (20.0 g., 0.1*M*), glycollic acid (15.2 g., 0.2*M*), and sodium (0.69 g., 0.03. g. atom) in 98% methanol (100 c.c.) was anodised by passing a current of 1.5 to 1.7 amps. for 8 hours (theoretical time, 5.36 hours). The internal temperature was maintained below 30°. The anodised solution was freezed and filtered. The residue (A) was kept separately and from the methanolic filtrate the solvent was removed under diminished pressure; the residue was dissolved in ether, washed with 2% NaOH, and finally with water. The ethereal layer was dried over anhydrous Na_2SO_4. The ether was removed and the residue carefully distilled till the temperature reached 275°. While the distillate (B) was kept separately, the residue was mixed with (A). This on distillation gave 10.8 g. of pure docasane[n], b.p. 220°/12 mm (lit. b.p. 224°/15 mm). The fraction (B) on refractionation gave 4.9 g. of ethylene glycol, b.p. 195-97° (lit. b.p. 197°) and 5.1 g. of lauryl alcohol, b.p. 150°/20 mm (lit. b.p 255-59°.). (Found: C,77.42; H, 13.93. Calc. for $C_{12}H_{26}O$: C,77.42; H, 13.98%). *p*-Bromobenzenesulphonyl, m.p. 49°; *p*-toluenesulphonyl, m.p. 30°.

Myristyl Alcohol.—A mixture of a solution of myristic acid (22.8 g., 0.1*M*), glycollic acid (15.2 g., 0.2*M*), and Na (0.69 g., 0.03 g.atom) in 98% methanol (150 c.c.) was anodised at 1.5 to 1.7 amps. for 8½ hours (theoretical time, 5.36 hrs). Internal temperature was kept between 30° and 35°. On working up the anodised solution as above, 8.3 g. of pure hexacosane[n], m.p. 60° (lit. m.p. 59-60°), 5.0 g. of ethylene glaycol, b.p. 91°/12 mm (lit b.p. 197°), and 5.3 g. of myristyl alcohol, b.p. 160-65°/10 mm (lit. b.p. 160°/10 mm) were obtained. (Found: C, 78.11; H, 14.01. Calc. for $C_{14}H_{30}O$: C, 78.5; H, 14.02 %). *p*-Toluenesulphonyl, m.p. 35°; *p*-bromobenzenesulphonyl, m.p. 51.5°. Some amount of the final residue, containing impure hexacosane[n], was also left. This was not further worked up.

Cetyl Alcohol.—A mixture of palmitic acid (25.6 g., 0.1*M*), glycollic acid (15.2 g., 0.2*M*), and Na (0.69 g., 0.03 g. atom) in 98% methonal (150 c.c.) was anodised at 1.5 to 1.17 amps. for 8 hours (theoretical time, 5.36 hrs.). The internal temperature of the cell was maintained between 40° and 50°. The anodised solution gave 14 g. of triacontane, m.p. 68° (lit. m.p. 68°), 5.7 g. of ethylene glycol, b.p. 91°/12 mm (lit. b.p. 197°), and 3.3 g. of cetyl alcohol, b.p. 178-83°/12 mm (lit. b.p. 190°/15 mm.). (Found: C, 79.7; H, 14.2. Calc. for $C_{16}H_{34}O$: C, 79.34; H, 14.05 %). *p*-Toluenesulphonyl, m.p. 37°.; *p*-bromobenzenesulphonyl, m.p. 54°. The residue (4 g.), which had not been further worked, was left in the flask.

dl-*Tridecanol*-2.—A mixture of lauric acid (10. g., 0.05*M*), lactic acid (9 g., 0.1*M*), and Na (0.35 g., 0.015 g. atom) in 98% methanol (75 c.c.) was anodised at 1.5 to 1.7 amps. for 5½ hrs. (theoretical time, 2.68 hrs.). Internal temperature was maintained between 25° and 30°. The anodised solution gave 4 g. of docosane[n], b.p. 218-20°/12 mm (lit. b.p. 224°/15 mm), 3.5 g. of butane-2,3-diol, b.p. 81-83°/12 mm (lit. b.p. 182.5°), and 2 g. of *dl*-tridecanol-2, b.p. 151-52°/12 mm (lit. b.p. 151°/11 mm). (Found: C, 77.61; H, 14.1. Calc. for $C_{13}H_{28}O$: C, 78.00; H,14.0%). *Acid phthalate*, m.p. 58-59°.

dl-*Pentadecanol*-2—A mixture of myristic acid (11.4 g., 0.05*M*), lactic acid (9 g., 0.1 *M*), and Na (0.35 g., 0.015 g. atom) in 98% methanol (100 c.c.) was anodised at 1.5 to 1.7 amps. for 6 hrs (theoretical time, 2.68 hrs.). Internal temperature was maintained between 30° and 35°. The anodised solution gave 4.2 g. hexacosane[11], m.p. 60° (lit. m.p. 59-60°), 3.4 g. of butane-2,3-diol, b.p. 81-83°/12 mm (lit. b.p. 182.5°), and 2.55 g. of *dl*-penta decanol-2, b.p. 163-65°/12 mm. (Found: C, 78.8; H, 13.71. $C_{15}H_{32}O$ requires C, 78.95; H, 14.03%). Acid phthalate, m.p. 57.58°. The final residue (3.4 g.) was not further worked up.

dl-*Heptadecanol*-2.—A mixture of palmitic acid (12.9 g., 0.05*M*), lactic acid(9.0 g., 0.1*M*), and Na(0.35. g., 0.015 g. atom) in 98% methanol (100 c.c.) was anodised at 1.5 to 1.7 amps. for 6 hrs. (theoretical time, 2.68 hrs.). Internal temperature was maintained at 40-50°. The anodised solution yielded 6.8 g. of triacontane, m.p. 68° (lit. m.p. 68°), 3.5 g. of butane-2, 3-diol, b.p. 81-83°/12 mm (lit. b.p. 182.5°), and 2.3 g. of *dl*-heptadecanol-2, b.p. 185-87°/2 mm (lit. b.p. 140°/0.5 mm). (Found: C, 79.20; H, 13.81. Calc. for $C_{17}H_{36}O$: C, 79.69; H, 14.07 %). Acid phthalate, m.p. 63°. The final residue (2.4 g.) was not further worked up.

CHEMICAL LABORATORIES,
D.A.V. COLLEGE, KANPUR.

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Anodic Synthesis. Part II. Homopilosinic Acid and *dl*-Homopilopic Acid

J. K. Mehrotra and A. N. Dey

Homopilosinic acid has been prepared by hydrolysis of the corresponding substituted butyric acid. In view of the difficulty in separating the mixture of isomeric acids obtained during the preparation of homologues of this acid, a method, partly based on electrolysis, has been employed with success.

Isopilocarpine, on oxidation with $KMnO_4$ (Jowett, *J. Chem. Soc.*, 1900, **77,** 474, 851; 1901, **79,** 581, 1331; Pinner, *ibid.*, 1903, **83,** 438; Pinner *et al.*, *Ber.*, 1900, **33,** 1424, 2357; 1901, **34,** 727; 1902, **35,** 204, 2443; 1905, **38,** 2560), gives a mixture of pilopic acid (X: R=Et) and homopilopic acid (VII a: R=Et). Pilopic acid and isopilopic acid were synthesised by Tschitschibabin and Preobrashenski (*Ber.*, 1930, **63,** 460) from diethyl formylsuccinate. Preobrashenske *et al.* (*Ber.*, 1936, **69,** 1835; *Bull. Acad. Sci., U. S. S. R.*, 1936, 993) converted *dl*-pilopic acid *via* pilopyl alcohol, chloride, and nitrile to *dl*-homopilopic acid. Preobrashsenski *et al.* (*Doklady, Acad. Nauk. S. S. S. R.*, 1951, **81,** 613), following the above procedure, have prepared several homologues of homopilopic acid.

Independently, Dey (*J. Chem. Soc.*, 1937,1057) had prepared *dl*-homopilopic acid (VIIa: R=Et) and *dl*-homoisopilopic acid (VIIa: R=Et) by condensing ethyl γ-phenoxycrotonate (I) with cyanoacetate and ethyl iodide and hydrolysing the substituted glutrate (II) formed.

$$\underset{\text{(I)}}{PhOCH_2CH{=}CH.COOH} \longrightarrow \underset{\text{(II)}}{\begin{matrix} PhOCH_2CH.CH_2COOEt \\ | \\ EtC(CN).COOEt \end{matrix}} \longrightarrow \text{(VIIa: R=Et)}$$

Dey also prepared these acids by condensing ethyl 2-chloro-3-phenoxybutyrate (III) with ethyl malonate and ethyl iodide and hydrolysing the condensed product (IV).

$$PhOCH_2CHCl.\ CH_2COOEt \longrightarrow PhOCH_2CH(EtC(COOEt)_2).CH_2COOEt \longrightarrow (VIIa: R=Et)$$

(III) (IV)

As the removal of the phenoxy group requires higher temperatures causing isomerisation of the acids, Dey replaced it by OEt group.

In the present investigation substituted butyric acids have been used for the preparation of homolactonic acids. For this purpose, 1-chloro-3-ethoxypropan-2-ol (Fairbrowne *et al.*, *J. Chem. Soc.*, 1926, 2318) was converted into 1-cyano-3-ethoxypropan-2-ol (Lespieau, *Compt. rend.*, 1905, **140,** 437) by boiling with ethanolic KCN. This was then dehydrated by P_2O_5 to 1-ethoxy-3-cyano-2-propene (V) (Lespieau, *ibid.*, p. 724) and the latter was finally condensed with diethyl malonate to obtain ethyl 1-ethoxycarbonyl 2-ethoxymethyl-3-cyanobutyrate (VI: R=H). On hydrolysis this gave homopilosinic acid (VIIa and VIIb: R=H).

$$CN.CH{=}CH.CH_2OEt \longrightarrow CN.CH_2CH(RC(COOEt)_2).CH_2COOEt$$

(V) (VI)

$$RCH(CO\text{-}O\text{-}CH_2).CH_2COOH \quad \text{and} \quad CH_2(CO\text{-}O\text{-}CH_2).CHR.COOH$$

(VIIa) (VIIIb)

To generalise this method for the preparation of homologues of this acid, the preparation of *dl*-homopilopic acid was attempted. For this purpose (VI: R=H) was condensed with ethyl iodide. Ethyl 1-ethoxycarbonyl-1-ethyl-2-ethoxymethyl-3-cyanobutyrate (VI: R=Et), thus produced, was hydrolysed, yielding two isomeric acids (VIIa and VIIb: R=Et.) The esters of these acids could be separated from each other with difficulty. The same difficulty arose when, instead of ethyl iodide, benzyl chloride was used. In this case the yields were found to be very poor.

In a further attempt for the preparation of these acids, a method partly based upon anodic synthesis (this *issue*, p.885) has been utilised. Thus for the preparation of ethyl homopilosinate (XI: R=H), first pilosinic acid (X: R=H) was prepared. Diethyl 1-ethoxycarbonyl-succinate (VIII: R=H) (Michael, *Ber.*, 1905, **38,** 3223) was condensed with monochloromethyl ethyl ether in dry benzene to produce diethyl 1-ethoxycarbonyl-1-ethoxymethyl-succinate (IX: R=H). The latter was hydrolysed to pilosinic acid (X : R=H). This, when electrolysed with ethyl hydrogen malonate, gave ethyl homopilosinate (XI: R=H) in 32.56% yield.

$$EtOOC.CHR.CH(COOEt)_2 \longrightarrow EtOOC.CHR.C(CH_2OEt)(COOEt)_2 \longrightarrow$$

(VIII) (IX)

$$RCH(CO\text{-}O\text{-}CH_2).COOH \longrightarrow RCH(CO.O.CH_2).CH_2COOEt$$

(X) (XI)

Similarly, for the preparation of ethyl *dl*-homopilosinate (XI: R=Et; yield 20%) by electrolysis, following analogous reactions but using diethyl 1-ethoxycarboxyl-2-ethylsuccinate (VIII: R=Et) (Bischoff and Hjett, *Ber.*, 1888, **21**, 2091), *dl*-pilopic acid (X:R=Et) was produced. This was then electrolysed with ethyl hydrogenmalonate. Thus electrolytic method has been found to be quite convenient for the preparation of this class of compounds, which are intermediates for the synthesis of the Jaborandi alkaloids.

EXPERIMENTAL

Ethyl 1-Ethoxycarbonyl-2-ethoxymethyl-3-cyanobutyrate.—To dry ethanol (100 c.c.) containing sodium (9.2 g.) was added diethyl malonate (80 g.). When the mixture had acquired the room temperature, 1-ethoxy-3-cyano-2-propene (45.5 g., b.p. 80-83°/15 mm) was added dropwise with stirring during 45 minutes. The mixture was gently refluxed for 1½ hours, cooled, and glacial acetic acid (25 g.) was added with stirring. After removal of the ethanol, the cooled residue was poured in 200 c.c. of water. The lower layer of the crude ester was separated and the aqueous layer extracted with $CHCl_3$. The combined organic liquid was dried over fused $CaCl_2$ and the solvent removed. The residue was fractionally distilled when after the forerun of diethyl malonate at 100°/20 mm, the bulk (105 g.) of ethyl 1-ethoxycarbonyl-2-ethoxymethyl-3-cyanobutyrate distilled at 192-99°/20 mm (b.p. 194-96°/20 mm); $d_{18.5}^{18.5}$ 1.0637; $n_D^{\text{co.9}}$ 1.439. (Found: C, 58.1; H, 8.5. $C_{13}H_{21}O_5N$ requires C, 57.56; H, 7.75%).

Homopilosinic Acid.—Ethyl 1-ethoxycarbonyl-2-ethoxymethyl-3-cyanobutyrate (60 g.) and HCl (conc., 120 c.c.) were gently refluxed for 8 hours on a low flame. The mixture was evaporated to dryness, water was added, and the whole was extracted with ether (30 c.c. × 2). The aqueous layer was treated with charcoal and again evaporated to dryness under diminished pressure. After desiccation for 24 hours, this was extracted with 50,40, 30,20, and 10 c.c. portions of ether, leaving NH_4Cl as the residue. The mixed ethereal layer was dried over anhydrous Na_2SO_4 and the solvent removed, when β-ethoxymethyl glutrate was obtained as a colorless viscous liquid (27g.), soluble in water and ether; n_D^{35} 1.448. (Found: C, 50.61; H, 8.6. $C_8H_{14}O_5$ requires C, 50.53; H, 7.9%). This formed an anhydride on heating. This compound (10.g.) was refluxed with 48% HBr (40 g.) for 6 hours and then evaporated to dryness under diminished pressure till completely free of HBr fumes. The residue, dissolved in water (50 c.c.), was treated with charcoal and the clear aqueous layer was reduced to a small bulk and kept in a refrigerator overnight when crystalline homopilosinic acid was obtained (6.5 g.). This was recrystallised from water, m.p. 85-86° (lit. m.p. 86.5°). The mother liquor further gave 1.5 g. of the same compound. This is soluble in water and ether. (Found: C, 50.03; H, 5.51. Calc. for $C_6H_8O_4$: C, 50.0; H, 5.56%). Ethyl homopilopiate, b.p. 153-56°/6 mm. (Found: C, 55.7; H, 7.2. Calc. for $C_8H_{12}O_4$: C, 55.8; H, 6.98%).

Ethyl 1-Ethoxycarbonyl-1-ethyl-2-ethoxymethyl-3-cyanobutyrate.—To sodium (4.6 g.), dissolved in ethanol (75 c.c.), taken in a 500 c.c. three-naked flask, ethyl 1-ethoxycarbonyl-2-ethoxymethyl-3-cyanobutyrate (54.2 g.) was added with stirring. This was followed by dropwise addition of ethyl iodide (46.8 g.). The whole was refluxed for 2 hours and the unchanged EtI and ethanol were removed. The residue was poured in water (150 c.c.), the ester layer separated, and the aqueous layer extracted with ether (50 c.c.). The ether layer was mixed with the ester and the mixture was dried over fused $CaCl_2$. The solvent was removed and the bulk of the butyrate (48 g.) was collected at 178-82°/6 mm; $d_{32.6}^{32.6}$ 1.0419; n_D^{34} 1.4405. (Found: C, 60.94; H, 8.84; N, 4.61. $C_{15}H_{25}O_5N$ requires C, 60.20;

H, 8.36; N, 4.68%). It is a light yellow liquid with characteristic odour of a nitrile; it is insoluble in water and soluble in organic solvents.

dl-*Homopilopic Acid*.—The above cyanobutyrate (30 g.) was refluxed with HCl (conc., 120 c.c.) for 12 hours and evaporated to dryness. The residue was kept in vacuum over solid KOH for 24 hours, extracted with dry ether, the ether removed, and the residue was refluxed with 48% HBr (40 c.c.) for 12 hours. HBr was completely removed under diminished pressure and the residual syrup (9 g.) containing a mixture of lactonic acids was kept over solid KOH in vacuum for several days. This was esterified with ethanol. The mixture of esters was fractionated and the fraction passing at 193-96°/4 mm, containing ethyl homopilopiate (lit. b.p. 210°/10 mm), was collected separately (7.5 g.). This fraction was refractionated several times. The ester thus obtained was hydrolysed by HCl (40 c.c.) to yield 5.9 g. of *dl*-homopilopic acid, m.p. 100°; b.p. 211-14°/4 mm (lit. m.p. 100-101°; b.p. 235-37°/20 mm). (Found: C, 56.6; H, 7.4. Calc. for $C_8H_{12}O_4$: C, 56.2; H, 7.07%).

Ethyl 1-*ethoxycarbonyl*-1-*benzyl*-2-*ethoxymethyl*-3-*cyanobutyrate* (b.p. 228-31°/2 mm) was prepared by using sodium (4.6 g.), ethyl 1-ethoxycarbonyl-2-ethoxymethyl-3-cyanobutyrate (54.2 g.), and benzyl chloride (38.0. g.) in 21.6 g. yield. (Found: C, 65.93; H, 7.48; N, 3.47. $C_{20}H_{27}O_5N$ requires C, 66.48; H, 7.48; N, 3.88%).

Attempted Method for 4-*Benzylhomopilosinic Acid*.—The above cyanobutyrate (25 g.) was first hydrolysed by HCl (conc., 130 c.c.). After removal of NH_4Cl, as described earlier, it was further hydrolysed by 48% HBr (40 g.). HBr was removed and the crude residue (3.9 g.) was esterified. From the mixture of esters no specific fraction could be obtained. (Found: C, 68.68; H, 6.70. $C_{15}H_{18}O_4$ requires C, 68.70; H, 6.82%).

Diethyl 1-*Ethoxycarbonyl*-1-*ethoxymethylsuccinate*.—Sodium powder (2.3 g.) in dry xylol (100 c.c.) was treated with diethyl 1-ethoxycarbonylsuccinate (24.6 g., b.p. 156-57°/15 mm) (lit. b.p. 156-58°/15 mm) with vigorous stirring. When the reaction had subsided and whole of the sodium had dissolved, monochloromethyl ethyl ether (14.2 g.) was added during 30 mins. and the mixture left overnight. It was refluxed for 3 hours. The cooled opaque reaction mixture was poured in water (50 c.c.). The organic layer was washed with water (10 c.c. × 2) and dried over fused $CaCl_2$. The solvent was removed and the residue fractionated. The ester was collected at 160-63°/8 mm, yield 25 g. (Found: C, 54.9; H, 8.02. $C_{14}H_{24}O_7$ requires C, 55.26; H, 7.90%).

Pilosinic Acid.—Diethyl 1-ethoxycarbonyl-1-ethoxymethylsuccinate (10 g.) was refluxed with HCl (conc., 40 c.c.) for 6 hours when a homogeneous mixture was produced. The mixture was evaporated to dryness, the residue refluxed with 48% HBr (20 c.c.) for further 6 hours, and HBr was completely removed. The residue was dissolved in water (50 c.c.) and extracted with benzene (20 c.c.). The aqueous layer after decolorisation and evaporation from a water bath gave a residue, which, when recrystallised from water, gave 4 g. of pilosinic acid, m.p. 58.9° (lit. m.p. 57.8°). (Found: C, 45.7; H, 4.84. Calc. for $C_5H_6O_4$: C, 46.15; H, 4.62%).

Diethyl 1-*Ethoxycarbonyl*-1-*ethoxymethyl*-2-*ethylsuccinate* (50 g., b.p. 155-60°/4 mm) was prepared by following a procedure similar to that described above, using 4.6 g. of sodium powder, 55.0 g. of diethyl 1-ethoxycarbonyl-2-ethylsuccinate and 28.4 g. of monochloromethyl ethyl ether. (Found: C, 57.83; H, 8.25. $C_{16}H_{28}O_7$ requires C, 57.63; H, 8.43%).

dl-*Pilopic acid* was obtained by hydrolysing the preceding ester (66.5 g.) with HCl and HBr, as described above, in almost quantitative yield, m.p. 90-91° (lit. m.p. 90-91°). (Found: C, 53.0; H, 6.21. Calc. for $C_7H_{10}O_4$: C, 53.16; H, 6.33%). The ethyl ester, b.p. 300° (lit. b.p. 299°).

Ethyl Homopilosinate (*Electrclytically*).—A mixture of pilopic acid (6.5 g.), ethyl hydrogenmalonate (13.2 g.), and metallic sodium (0.35 g.) was electrolysed in methanolic solution, using the apparatus and procedure described in the previous communication (*loc. cit.*). A current of 1.5 amps. was passed for 3 hours and 30 minutes (theoretical time, 2.6 hours). The temperature of the reaction mixture was kept below 30°. The electrolysed solution yielded 4.2 g. of diethyl succinate, b.p. 217° (lit. b.p. 217°; by simple coupling), 2 g. of the residue, which had not been further worked up, and 2.8 g. of ethyl homopilosinate, b.p. 153-55°/6 mm (by cross coupling). (Found: C, 55.61; H, 6.83. Calc. for $C_8H_{12}O_4$: C, 55.81; H, 6.98%). Homopilosinic acid, m.p. 85-86° (lit. m.p. 86.5°).

Ethyl dl-*Homopilopiate* (*Electrolytically*).—A mixture of pilopic acid (15.8 g.), ethyl hydrogenmalonate (26.4 g.), and sodium (0.69 g.) in methanol was electrolysed by passing a current of 1.5 amps. for 7 hours (theoretical time, 5.3 hours). The temperature was kept below 30°. The electrolysed solution gave 9 g. of diethyl succinate, b.p. 217° (lit. b.p. 217°), 7 g. of the residue which was not further worked up, and 5.1 g. of ethyl *dl*-homopilopitate, b.p. 193-96°/4 mm (lit. b.p. 210°/10 mm.). (Found: C, 59.7; H, 7.9. Calc. for $C_{10}H_{16}O_4$: C, 60·0; H, 8.0 %). *dl*-Homopilopic acid, m.p. 100° (lit. m.p. 100-101°).

Chemical Laboratories,
D.A.V. College,
Kanpur.

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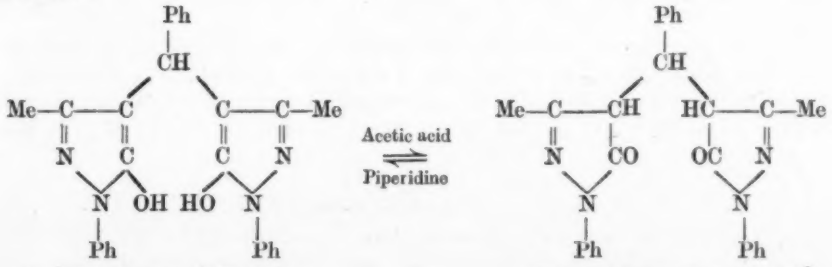
Tautomeric Products of Condensation of Aromatic Aldehydes with Pyrazolone

A. S. Mitra and M. K. Rout

Three products have been obtained by the condensation of aromatic aldehydes under different conditions with a 5-pyrazolone containing a reactive methylene group. The two bis-pyrazolone compounds are keto-enol tautomeric forms; one form shows carbonyl group absorption at 5.75μ in I.R. and the other form shows no peak between 5μ and 6μ. *p*-Dimethylaminobenzaldehyde produces the same product under different conditions.

Several condensation reactions take place at the active methylene group of 5-pyrazolone. Orthoformic ester, formamide, or chloroform-alkali condenses with 3-methyl-1-phenyl-5-pyrazolone to furnish 4,4′-methenyl-bis-(3-methyl-1-phenyl-5-pyrazolone) (Perroncito, Attix Congr. Internaz. Chem., 1938, III, 267-276). Aromatic aldehydes react with pyrazolones containing active methylene group, e.g., the formation of tautomeric products by condensation with 3-methyl-1-phenyl-5-pyrazolone (Porai and Malikova, *Izvest. Akad. Nauk, S. S. S. R., Otdel Khim. Nauk*, 1948, 519). It appears from available literature that the products of reaction of aromatic aldehydes with pyrazolone under different conditions has not been fully studied. In the present investigation, the reaction of benzaldehyde and substituted benzaldehydes in acidic, alkaline, and neutral media has been studied. The formation of mono-heterocyclic or bis-heterocyclic products is found to be governed by the nature of the medium.

Benzaldehyde reacts with 3-methyl-1-phenyl-5-pyrazolone in acetic acid solution to afford two products—red crystals of 4-benzylidene-3-methyl-1-phenyl-5-pyrazolone, m.p. 107° and pale yellow crystals of benzylidene-4,4′-bis-(3-methyl-1-phenyl-5-pyrazolone), m.p. 161-63°. Reaction of benzaldehyde with parent pyrazolone in ethanolic medium in presence of piperidine produces only one product, a colorless crystalline compound, m.p. 203-205°. This last product is converted to the above pale yellow crystals, m.p. 161-63°, when its ethanolic solution is treated with dilute sulphuric acid or the solid is treated with glacial acetic acid. Refluxing of the product (m.p. 161-63°) with piperidine in ethanolic medium regenerates the product, m.p. 203-205°. Refluxing with piperidine in the same medium also converts the red crystalline product, m.p. 107°, to the colorless product, m.p. 203-205°.

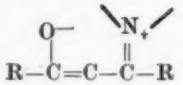


(Enol: m.p. 203-205°) (Carbonyl form: m.p. 161-63°)

No reaction, however, occurred between the parent pyrazolone and benzaldehyde in absence of any catalyst in rectified spirit even after keeping for two days.

The above compound, m.p. 203-205°, shows enolic character in giving violet coloration with ferric chloride solution. It forms a sodium salt and it gives a dimethoxy derivative.

The I. R. spectrum of the carbonyl form shows peak at 5.75μ and the enol form shows no peak between 5μ and 6μ. The spectrum of the enol, taken in the solid state in Nujol, shows no absorption for free or associated hydroxyl groups. Possibly there is intramolecular salt formation between the enolic hydroxyl group and a basic group present in the molecule. Similar possibility has earlier been suggested to explain the spectrum of β-amino-$\alpha\beta$-unsaturated ketones which contain an enolisable carbonyl group. In this case it has been suggested that the structure



is possible (Cromwell *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 3337).

Attempt has been made to obtain the benzylidenemonopyrazolone from the bis-pyrazolone compound by treatment with strong acid. Refluxing with EtOH-HCl of either of the two bis-pyrazolone compounds, however, produced a colorless crystalline hydrochloride, m.p. 235-40°. The hydrochloride on treatment with sodium acetate in aqueous ethanolic solution produced the bis-carbonyl compound, m.p. 161-63°.

EXPERIMENTAL

Condensation of Aromatic Aldehydes with 3-Methyl-1-phenyl-5-pyrazolone

To pyrazolone (0.5 g.), dissolved in glacial acetic acid (2 c.c.) at room temperature, benzaldehyde (0.4g.) was added to the solution and the mixture was kept at room temperature for 12 hours. It was then diluted with water till slight turbidity appeared. After one hour red monoclinic crystals, m.p. 107°, were filtered, yield 0.2 g. (Found: C, 77.6; H, 5.5. $C_{17}H_{14}ON_2$ requires C, 77.3; H, 5.34%).

The mother liquor from the above red crystals was diluted with four volumes of water when a precipitate appeared. This was filtered and crystallised twice from acetic acid and finally it was obtained as a pale yellow crystalline substance, m.p. 161-63°, yield 0.2 g. (Found: C, 74.62; H, 5.9. $C_{27}H_{24}O_2N_4$ requires C, 74.48; H, 5.35%).

Bis-diol.—3-Methyl-1-phenyl-5-pyrazolone (0.5 g.) was dissolved in absolute ethanol (10 c.c.) and benzaldehyde (0.4 g.) was added followed by piperidine (5 drops). The mixture was left at room temperature and crystals started separating after five minutes. These were filtered after 12 hours, m.p. 203-205°. (Found: C, 74.11; H, 5.71. $C_{27}H_{24}O_2N_4$ requires C, 74.48; H, 5.35%).

The Hydrochloride.—Solution of the benzylidene-bis-diol was made in 30% EtOH-HCl by warming on a water bath. On cooling the solution, crystals of the hydrochloride, m.p. 235-40°, separated. All the three benzylidenepyrazolones gave the same product

by the above treatment. Ethanolic solution of the hydrochloride is acidic to litmus and develops a violet colour with ferric chloride solution. Its aqueous extract gave no turbidity with silver nitrate solution, but it gave silver chloride on refluxing with ethanolic silver nitrate solution. It is soluble in aqueous sodium hydroxide solution. (Found: C, 62.9; H, 5.3. $C_{27}H_{26}O_2N_4Cl_2$ requires C, 63.65; H, 5.1%).

Conversions of Benzylidenemonopyrazolone and the Bis-pyrazolone

Benzylidenemonopyrazolone, m.p. 107°, was dissolved in rectified spirit; a few drops of piperidine were added and the mixture was refluxed on a water bath for 1 hour. White crystalline solid, m.p. 203-205°, separated from the hot solution. Mixed m.p. of the above product with benzylidene-bis-diol was not depressed.

The bis-diol was dissolved in a minimum volume of glacial acetic acid at room temperature and left overnight. Water was added next day till turbidity appeared. A pale yellow crystalline solid was collected after 1 hour, m.p. 161-63°.

The conversion of the enol to carbonyl could also be carried out in the following manner. To the bis-diol, dissolved in 10% aqueous NaOH at room temperature, solid ammonium chloride was added and the mixture was warmed when a precipitate came down. It was crystallised from aqueous ethanol, m.p. 161-63°. Refluxing with either ammonia or pyridine in ethanolic solution did not convert the carbonyl compound to the enolic tautomer.

Methoxy Derivative of Diol

To benzylidene-4,4′-bis-(3-methyl-1-phenyl-5-pyrazolone) (1 g.), dissolved in aqueous NaOH (0.2 g. in 10 c.c.), dimethyl sulphate (0.25 g.) was added. The mixture was refluxed on a water bath for 2 hours, extracted with ether, and the extract was washed with water and dried over anhydrous sodium sulphate. Ether was removed and the residue was crystallised from acetone as granular, colorless crystals, m.p. 179°.

The above product gave no coloration with ferric chloride. It is insoluble in aqueous alkali. (Found: C,75.04; H, 5.7. $C_{29}H_{28}O_2N_4$ requires C, 75.01; H, 6.03%).

MAYURBHANJ CHEMICAL LABORATORY,
RAVENSHAW COLLEGE,
CUTTACK.

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Study on the Citrate Complex of Strontium

Rabindra K. Pattnaik and S. Pani

The citrate complex of strontium has been investigated by the *p*H titration method at *p*H 7.2 to 7.3. The equilibrium constant of the reaction:

$$Sr^{2+} + Cit^{3-} \rightleftharpoons SrCit^{-}$$

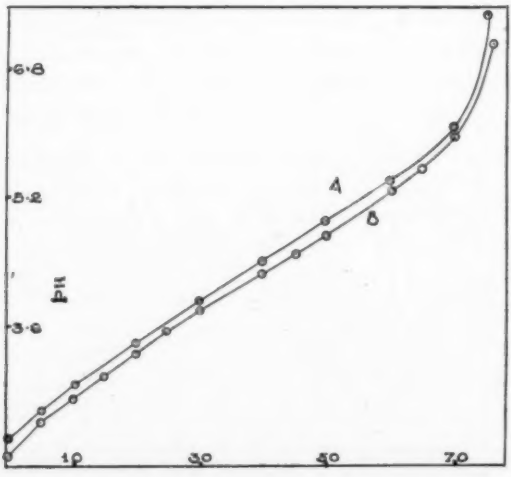
is determined to be 5.23×10^2.

Hastings and co-workers (*J. Biol. Chem.*, 1934, **107**, 351) found the formation constant of strontium citrate by biological assay method to be 5.012×10^2. Schubert and Richter (*J. Amer. Chem. Soc.*, 1948, **70**, 4259) studied the strontium citrate complex by using cation exchangers and found the formation constant of $SrCit^-$ to be 6.457×10^2.

EXPERIMENTAL

An *M*/20 strontium perchlorate solution was prepared as follows. A very pure sample of strontium carbonate was added in excess to an *M*/10 perchloric acid so that some of the strontium carbonate was left undissolved. The solution was boiled for a few minutes at 40-50° to remove CO_2. The solution was cooled and allowed to settle for 3 to 4 hours for attaining equilibrium. Finally the solution was filtered to a dry bottle and the filtrate estimated for strontium content.

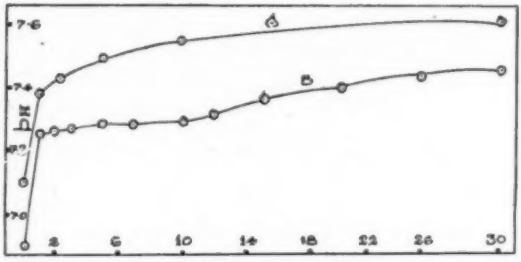
Expt. I.—Curve A (Fig. 1) represents the results obtained by titrating 200 c.c. of a solution containing 0.025 g. mole of citric acid and curve B represents that of another solution of the same volume containing 0.025 g. mole of citric acid and 0.0025 g. mole of strontium perchlorate against *N*-NaOH at 32.5°.



N-NaOH *added* (*c.c.*).

FIG. 1

Expt. II.—Curve A (Fig. 2) represents the results obtained by titrating 100 c.c. of a solution containing 0.025 g. mole of sodium perchlorate and curve B that of another 100 c.c. of a solution containing 0.025 g. mole of sodium perchlorate and 0.00125 g. mole of strontium perchlorate against 0.1*M* sodium citrate at 32.5°.



Na-*citrate added* (*c.c.*).
FIG. 2.

Sodium perchlorate was added to maintain a constant ionic strength in both the solutions.

TABLE I

*p*H.	$[Ct]_A$ or $[Cit^{3-}]_A \times 10^4$.	$[Ct]_B \times 10^3$.	$[Sr(ClO_4)_2] \times 10^2$.	$[SrCit^-] \times 10^3$.	$[Sr^{2+}] \times 10^3$.	$K \times 10^{-2}$.
7.25	3.985	0.9902	1.238	0.5917	11.79	1.260
7.26	4.976	1.9610	1.226	1.4640	10.80	2.725
7.26	4.976	2.9130	1.213	2.4160	9.71	5.000
7.27	4.976	3.6610	1.204	3.1640	8.88	7.161
7.27	5.474	4.7620	1.191	4.2150	7.69	10.000

DISCUSSION

The results obtained in expt. I are similar to those obtained in the calcium citrate systems (Pattnaik and Pani, this *Journal*, 1961, **38**, 229). There is no indication of liberation of acid. The formation of the complex resulting in removal of the citrate ion is, however, indicated. The horizontal distance between the two curves increases in the beginning, then decreases, and finally becomes negligible after *p*H 6.0.

In expt. II the results are again similar to those obtained in the calcium citrate system (*loc. cit.*). There is an appreciable rise in this case also in the *p*H after the addition of very nearly 1 g. mole of sodium citrate per g. mole of strontium perchlorate. This is a clear indication of the formation of $SrCit^-$, which is a stable complex.

Calculation of the Equilibrium Constant

In expt. II the complex $SrCit^-$ is formed with increasing addition of sodium citrate. The formation of the complex is nearly complete when 1 g. mole of sodium citrate is added

per g.atom of strontium. The reaction is represented by equation (1) and the equilibrium constant by equation (1-1)

$$Sr^{2+} + Cit^{3-} \rightleftharpoons SrCit^{-} \quad .. \quad (1)$$

$$\frac{[SrCit^{-}]}{[Sr^{2+}] \times [Cit^{3-}]} = K \quad .. \quad (1\text{-}1)$$

$[Ct]_A$, $[Ct]_B$, $[Sr(ClO_4)_2]$, $[SrCit^{-}]$, $[Cit^{3-}]$ and $[Sr^{2+}]$ were calculated as determined in the case of calcium citrate complex (*loc. cit.*) and formation constant of $SrCit^{-}$ from Sr^{2+} and Cit^{3-} was calculated by equation (1-1). The values are recorded in Table I.

The mean value of K is 5.23×10^2. This is in good agreement with the values obtained by many authors.

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Department of Chemistry,
University College of Engineering,
Burla.

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Volumetric Estimation of Malonates by Oxidation with Iodine

R. M. Verma and Sameer Bose

A procedure is described for volumetric determination of malonate ion, based on its reaction with known excess of standard iodine solution at 100° and titrating the residual iodine with a standard hypo solution. The procedure is applicable to neutral malonate solutions containing 15 to 80 mg. of malonic acid with a precision of 1% or more. The interference caused by salts of organic acids and other organic substances has also been investigated.

Cameron and McEwan (*Proc. Chem. Soc.*, **26**, 176) determined malonic acid by heating it with an excess of potassium permanganate and then estimating the amount of unused oxidant. The product of the reaction is formic acid which is not further oxidised. In the present method iodine solution has been utilised as the oxidising agent.

According to Nylén (*Kgl. Norske. Videnskab. Selskabs. Skrifter*, 1938, **2**, 19) under certain conditions iodine reacts with malonic acid to substitute iodine for hydrogen of CH_2 group and under other conditions the -CHI-group is reduced to CH_2 group by iodide ion and free iodine is formed. He also found that at pH <1 practically no iodine reacted with malonic acid, but at pH >5 an amount corresponding to the following reaction was consumed.

$$CH_2(COOH)_2 + I_2 = ICH(COOH)_2 + H^+ + I^-$$

In the present method, neutral malonate solution is heated with a known excess of standard iodine solution for a considerable time in a flask fitted with a glass-joint water condenser to prevent iodine from escaping. One of the products of the reaction is iodoform. It is also found that for every molecule of malonic acid, 4 atoms of iodine are consumed. Knowing the amount of iodine consumed, the quantity of malonic acid present is calculated. Although the consumption of iodine is quantitative, the exact course of the reaction resulting in the formation of iodoform is not known. Further investigation in this connection is in progress.

$$[CH_2(COOH)_2 \equiv 2I_2 \equiv 4Na_2S_2O_3]$$

$M/10$ iodine (1 c.c.) consumed=5.2 mg. of malonic acid.

EXPERIMENTAL

Sodium hydroxide, sodium thiosulphate, iodine, and starch used were of A.R. quality. Potassium iodide was of E. Merck's variety and malonic acid was of Johnson. 0.1M Iodine solution (containing 50 g. KI per litre), 0.1N and 0.05N hypo, 0.1N-NaOH, and 1% aqueous starch solutions were prepared. Standard solutions of sodium malonate were prepared by adding the calculated amount of sodium hydroxide solution to standard malonic acid solutions.

Procedure.—A neutral malonate solution (5 to 15 c.c.) containing 15 to 80 mg. of malonic acid was pipetted into a 250 c.c. flask, a known excess (6 times) of the standard iodine solution was added, and the total volume was made 70 to 100 c.c. with distilled water. A 3 feet long water condenser with ground-glass joint was attached to the flask which was kept in an electrically operated water bath containing water at 25°. The upper end of the condenser was closed loosely by inverting over it a 50 c.c. beaker. The water bath was switched on, the time required for boiling to start was about 20 minutes; 20 minutes more were allowed after start of boiling so that the total period of heating was 40 minutes after which the flask along with the condenser was taken out of the bath and cooled. Then the condenser was thoroughly washed with a 5% KI solution so as to completely transfer the iodine particles, sticking to the condenser wall, into the flask. The residual iodine was titrated with the standard hypo solution. A blank was also carried out in a similar manner except for the addition of malonate solution; the difference between the two thio readings gave the amount of iodine consumed. The results for the evaluation of different amounts of malonates, as recorded in Table I, show that the precision of the method is 1% or more. All the estimations were carried out in duplicates. It was found in the blank experiment that the amount of iodine lost on heating in the manner described above was negligible (less than 0.1%).

TABLE I

Malonic acid						
	Present (mg.)	78.00	62.40	52.00	41.6	26.00	15.60
	Found mg.)	78.26	62.53	51.87	41.6	25.74	15.47
	%Error	+0.4	+0.3	−0.3	±0.0	−1.0	−1.0

Effect of change in the amount of water, in the period of heating, and in the concentration of iodine solution was also studied. The results are recorded in Tables II and III. Satisfactory results were found when 45 c.c. of water was added to 26 mg. of malonic acid in a total volume of 70 c.c.

If the total volume is less than 55 to 60 c.c., low results for malonate are obtained. In order to get accurate results, the total volume should be kept between 70 and 100 c.c. for about 25 mg. of malonic acid.

Effect of Increase in the Concentration of Iodine.—Several experiments were carried out taking different amounts of sodium malonate with a view to studying the effect of change in the amount of iodine. Accurate results were obtained when for every molecule of malonic acid 6 molecules (~) of iodine were added. If malonic acid present was 15 to 45 mg., even a larger excess (10 molecules of iodine per molecule of malonic acid) did not affect the results, but in presence of 45 to 80 mg. of malonic acid larger excess of iodine afforded higher values for malonate.

Total period of heating for 30-45 minutes proved sufficient for completion of the reaction (Table II).

Interference.—The interference caused by salts of other organic acids and organic substances has been studied and shown in Table III. Sodium formate and acetaldehyde cause profound interference and all the added iodine is consumed. Ethanol, methanol,

sodium acetate, calcium gluconate, calcium lactate, sodium tartrate, and sodium benzoate do not interfere with the present procedure.

TABLE II

Effect of increase in the period of boiling.

M/20 Malonic acid solution (5 c.c.) +5 c.c. of *N*/10-NaOH solution+15 c.c. of *M*/10 iodine solution+60 c.c. water. Time required for boiling to start=20 mins.

Heating time after start of boiling.	Total period of heating.	Malonic acid. Present.	Malonic acid. Found.	%Error.
10 mins.	30 mins.	26.0 mg.	25.87 mg.	−0.5
25 (recommended)	45	,,	25.93	−0.3
40	60	,,	26.00	±0.0
70	90	,,	25.93	−0.3
100	120	,,	25.87	−0.5

TABLE III

Sodium malonate solution (5 c.c.)+15 c.c. of *M*/10 iodine solution+50 c.c. water. Total volume=70 c.c. Time heating =40 minutes. Malonic acid added=26.0mg.

Expt. No.	Substance added (do not interfere).		Malonic acid found.	% Error.
1.	Ethyl alcohol	(0.2 g.)	26.00 mg.	±0.0
2.	Methyl alcohol	,,	26.00	±0.0
3.	Na-acetate	,,	26.26	+1.0
4.	,, benzoate	,,	26.00	±0.0
5.	,, tartrate	,,	26.00	±0.0
6.	Ca-gluconate	,,	26.26	+1.0
7.	,, lactate	,,	26.13	+0.5
8.	,, butyrate	,,	26.13	+0.5
9.	Benzaldehyde	,,	26.13	+0.5
Substances interfere.				
10.	CCl_4	,,	26.52	+2.5
11.	K-citrate	,,	26.91	+3.8
12.	Glucose	,,	29.38	+13.6
13.	Formaldehyde	,,	32.24	+24.0
14.	Salicyladehyde	,,	37.83	+30.0
15.	Na-oxalate	,,	56.03	+115.5
16.	,, salicylate	,,	55.90	+115.0
17.	,, borate	,,	50.83	+95.5
18.	,, phthalate	(containing 0.2g.	27.04	+4.0
19.	,, adipate	of acid)	27.60	+6.5
20.	,, aminoacetate	,,	29.64	+14.0
21.	,, phenylacetate	,,	26.78	+3.0
22.	,, maleate	,,	36.92	+42.0
23.	,, malate	,,	26.91	+3.5
24.	,, fumarate	,,	28.34	+9.0

The present procedure is an improvement over that described by Cameron and McEwan in its precision and applicability in presence of many other organic compounds. Tartaric acid interferes with the procedure of Cameron and McEwan, whereas the present procedure is not interfered by its presence.

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Department of Chemistry,
Mahakoshal Mahavidyalaya,
Jabalpur.

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Determination of Zeta-potential of Quartz Particles in Dilute Solutions of KCl

Charu Bhusan Roy

True zeta-potential of quartz particles of graded size in dilute KCl solutions has been measured by electro-osmotic and sedimentation potential methods. The values obtained by the former is 124 mv and that by latter, 133 mv, the agreement between the two being satisfactory; the mean value of ζ is taken as 129 mv.

Bull and Gortner (*J. Phys. Chem.*, 1932, **36**, 111) by using the streaming potential method measured the zeta-potential of sintered quartz particles forming a diaphragm and found the magnitude of the potential to decrease with the decrease in size of the particles forming the diaphragm. Wood (*J. Amer. Chem. Soc.*, 1946, **68**, 432) attributed this variation to the effect of the decrease in radius of the pores relative to the thickness of the double layer with decreasing particle size. The equation deduced by him is represented as

$$\eta \frac{HK}{P} = M - \frac{1}{2a} \Sigma_i \, d_i \triangle M_i \qquad \ldots \qquad (1)$$

where H is the streaming potential at a pressure P; M and d are the moment and the thickness of the double layer respectively and a is the radius of the pores of the diaphragm. Ghosh and co-workers (this *Journal*, 1953, **30**, 601) have, however, shown that the observations of Bull and Gortner can be accounted for quantitatively by an equation derived by taking the effect of surface conductance of the quartz particles into consideration. Their equation can be expressed as

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + \frac{m}{r} \qquad \ldots \qquad (2)$$

where ζ and ζ_a are true and apparent zeta-potentials respectively, r, the radius of the particles, and m is a constant under the condition of the experiment and includes surface conductance.

In view of the facts mentioned above, an attempt has been made by the present author to determine the true zeta-potential of quartz particles of graded size in dilute solutions of KCl by two methods, namely, the electro-osmotic and the sedimentation potential methods.

EXPERIMENTAL

A quartz sample, previously ignited at 1000°, was broken into pieces and ground in an agate mortar and sieved to obtain particles of a definite size. The first three samples were prepared by standard sieves and the last one by sedimentation of a fine suspension

in water. Each sample was boiled with aqua regia, washed with conductivity water, and finally ignited in an electric furnace at 800°.

Electro-osmotic Experiment

Electro-osmotic measurements were carried out in the usual manner as described by Mukherjee (this *Journal*, 1927, **4**, 461). A sample in sufficient amount was transferred to the same U-tube so that particles forming the diaphragm occupied a definite volume, care being taken that the sediment in the U-tube settled firmly in order to prevent its moving with the liquid. The particles in the diaphragm were washed by percolation with a solution of KCl of the desired concentration until conductance of the wash liquid was the same as that of the KCl solution used. Four such diaphragms, each with a particular sample, were made and electro-osmotic experiments were carried out with KCl solutions of the desired strength. From these data the values of apparent zeta-potential, ζ_a, were calculated using Smoluchowski's equation. A plot of $1/\zeta_a$ against $1/r$ gave a straight line. From the intercept of the straight line on $1/\zeta_a$ axis, the true zeta-potential, ζ, was found. The value of r used was the mean of that of the smallest and the largest of the particles in a given sample. The sieves were so selected that the difference in size between the smallest and the largest particles in a given sample was quite small. The results are recorded in Tables I and II.

TABLE I

Solution $=1\times10^{-5}$ *M*-KCl. Sp. conduc. $=2.82\times10^{-6}$ ohm^{-1}. Temp. $=30°$.

Size range ($r\times10^4$ cm).	(Mean) $1/r\times10^{-1}$.	ζ_a.	$1/\zeta_a$.
124-152	7.25	80 mv	0.0125
89-105	10.30	69	0.0145
56-76	15.20	58	0.0172
41-49	22.20	47	0.0213

ζ found from intercept (vide Fig. 1) on $1/\zeta_a$ axis is 124 mv.

TABLE II

Solution $=3\times10^{-5}$ *M*-KCl. Sp. conduc. $=6.1\times10^{-6}$ ohm^{-1}. Temp. $=30°$.

Size range ($r\times10^4$ cm).	(Mean) $1/r\times10^{-1}$.	ζ_a.	$1/\zeta_a$.
124-152	7.25	86.0 mv	0.0116
89-105	10.30	81.0	0.0123
56-76	15.20	74.5	0.0134
41-49	22.20	65.0	0.0154

ζ found from interecept (vide Fig. 1) on $1/\zeta_a$ axis is 104 mv.

Measurement of Sedimentation Potential

The sedimentation cell used was similar to that designed by Quist and Washburn (*J. Amer. Chem. Soc.*, 1940, **62**, 3169). Doubly distilled water of about 1×10^{-6} ohm^{-1} conduc-

tance was used throughout the experiment. KCl sample was Merck's guaranteed reagent. Two samples of quartz particles of mean radius 195μ and 97μ were used. Each sample was washed with conductivity water, then dried, and weighed. It was then shaken several times with KCl solution or water, as the case was, and finally transferred quantitatively to the reservoir of the cell containing the solution for a particular experiment. Silver-silver chloride electrodes were prepared by Brown's method (*ibid.*, 1934, **56**, 646). Sedimentation potential was determined with the help of a potentiometer and a thermionic amplifier (Leeds and Northrup, No. 7673). The steady value of potential was determined after allowing the particles to fall for a short time. Correction for asymmetric potential (if any) of the electrodes in absence of falling particles was made in each case. For the calculation of ζ, the procedure adopted by Quist and Washburn (*loc. cit.*) was followed. Specific conductance of the liquid medium was separately measured by conductivity measuring bridge. Dielectric constant and viscosity of the liquid for the corresponding temperature of the day's experiment were taken from the standard table. The results are recorded in Table III.

TABLE III

ζ by sedimentation potential method.

Temp. $=30^\circ \pm 1^\circ$.

Size range.	Mean size.	Conc. of electrolyte.	Conduc. of soln. $\times 10^6$ ohm^{-1}.	Amount bet. electrodes.	Potential developed.	Zeta-potential.
89-105μ	97μ	$0.5\times 10^{-5}M$	1.88	0.88 g.	5.2 mv	134 mv
		1.0	2.90	0.97	3.7	133
178-211μ	195	0.0	0.97	1.17	13.7	128
		0.5	2.04	1.13	6.6	134
		1.0	2.95	1.03	4.1	134

DISCUSSION

Tables I and II show that the value of apparent zeta-potential (ζ_a) for a given solution of KCl varies with the size of the quartz particles forming the diaphragm; the larger the radius of the particles forming a diaphragm, the larger is ζ_a. This observation is in agreement with the data reported by Bull and Gortner (*loc. cit.*) by the streaming potential method. It will also be noticed from Fig. 1, that a plot of $1/\zeta_a$ against $1/r$ gives a straight line in agreement with equation (2). The values of true zeta-potential of quartz particles found from the intercepts on $1/\zeta_a$ axis are 124 mv and 104 mv in contact with 1×10^{-5} *M*-KCl and 3×10^{-5} *M*-KCl solutions respectively. The data obtained by the sedimentation potential method (Table III) show that for particles of mean radius 97μ, the values of zeta-potential in contact with 0.5×10^{-5} *M* and 1×10^{-5} *M*-KCl solutions are 134 and 133 mv respectively. For particles of mean radius 195μ, the values of ζ_a for the same solutions of KCl, as given above, are 134 mv and 134 mv respectively. In contact with water, however, the value of ζ_a (particles of mean radius 195μ) is 128 mv. This value is somewhat lower than those found in contact with the solutions of KCl. This slightly low value is very probably due to the effect of surface conductance.

Ghosh *et al.* (this *Journal*, 1955, **32**, 29) have shown that the electrophoretic equation of Booth (*Trans. Faraday Soc.*, 1948, **44**, 455) and Henry (*ibid*, 1948, **44**, 1021) can be expressed in the following form when κr is large (where r is the radius of the particle and κ, the reciprocal of the thickness of electrical double layer):

$$\frac{1}{\zeta_a} = \frac{1}{\zeta}\left(1 + \frac{\chi}{S.r}\right) \quad .. \quad (3)$$

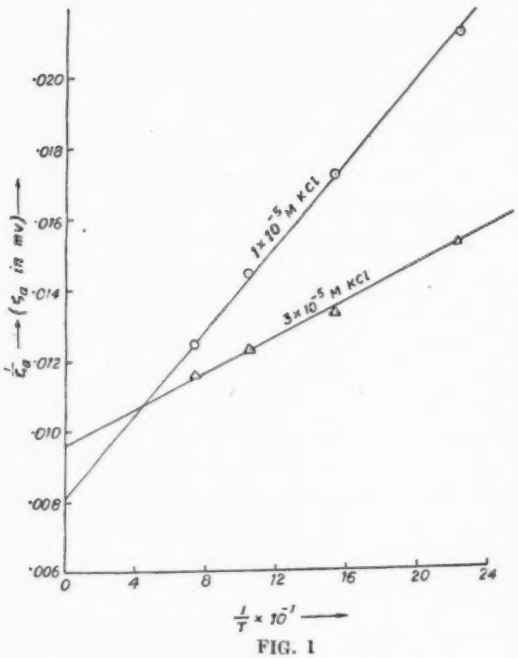

FIG. 1

The value of χ for jena 16111 (Rutger and de Smet, *Trans. Faraday Soc.*, 1947, **43**, 102) in KCl solution (c=0·20μ eqv./litre) and pyrex (Wijga, thesis, Utrecht, 1945, p.49) in KNO_3 solution (c=9.3—22.1 μ eqv./litre) is $\sim 1\times10^{-9}$ ohm^{-1}. So if the value of χ (sp. surface conductance) is assumed to be of the order of 10^{-9}ohm^{-1} for quartz particles, for S (sp. conductance of solution) $=3.0\times10^{-6}$ ohm^{-1} and radii 195μ and 97 μ, the values of true zeta-potentials calculated with the help of the above equation are respectively 1.5% and 3% greater than the values of ζ_a. Under conditions similar to that mentioned above, the correction for surface conductance to ζ_a, determined by sedimentation potential method, is expected to be of the same order of magnitude and will thus be small. The values of ζ_a obtained by using particles of mean radius 97μ and 195μ in contact with 1×10^{-5} *M*-KCl do not differ appreciably and this also confirms the conclusion mentioned above.

The values of true zeta-potential for quartz in contact with 1×10^{-5} *M*-KCl solution obtained by electro-osmotic and sedimentation potential methods are 124 and 133 mv respectively. Considering the limits of error possible in these experiments, the agreement between the two values may be considered fairly satisfactory. We may therefore take the mean of the two values 129 mv as the true zeta-potential of quartz in contact with 1×10^{-5} *M*-KCl solution.

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Department of Physical Chemistry,
University Colleges of Science & Technology,
Calcutta-9.

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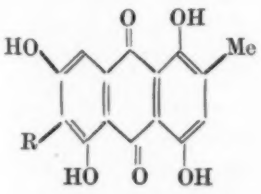
Synthesis of 6-Hydroxycatenarin, 1, 4, 7, 8-Tetrahydroxy-2-methylanthraquinone, and Helminthosporin

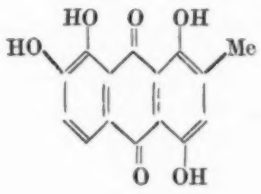
K. Chandrasenan, S. Neelakantan, and T. R. Seshadri

6-Hydroxycatenarin, 1,4,7,8-tetrahydroxy-2-methylanthraquinone, and helminthosporin have been synthesised following possible paths of biogenesis and involving *para* nuclear oxidation at the appropriate benzoylbenzoic acid stage.

Anthraquinone pigments with *para*-dihydroxy grouping have been isolated frequently as fungal metabolic products, e.g., helminthosporin, islandicin, catenarin, etc. In connection with the biogenesis of naturally occurring anthraquinones, it has been suggested (Aghoramurthy and Seshadri, *J. Sci. Ind. Res.*, 1954, **13A**, 114; Neelakantan and Seshadri, *ibid.*, 1960, **19A**, 71) that *para* nuclear oxidation (hydroxylation) forms a stage in their evolution and that this oxidation probably takes place in a pre-anthraquinone stage like the benzoylbenzoic acid. Following this, the preparation of 2-methylquinizarin, islandicin, cynodontin (Neelakantan *et al.*, *Proc. Ind. Acad. Sci.*, 1959, **49A**, 234), catenarin, and erythroglaucin (Chandrasenan *et al.*, *ibid.*, 1960, **51A**, 296) from the appropriate benzoylbenzoic acids has already been reported. In continuation of this work, the synthesis of 6-hydroxycatenarin (I), 1,4,7,8,-tetrahydroxy-2-methylanthraquinone (II), and helminthosporin (III) has been effected and the results are reported in this paper.



(I: R=OH)
(IV)=(I: R=H)



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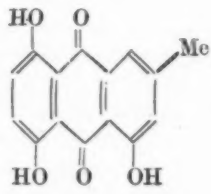
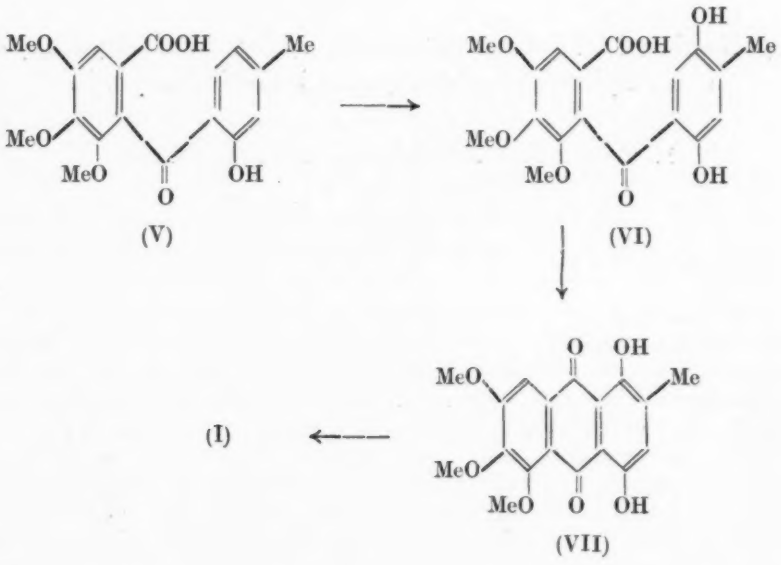


(III)

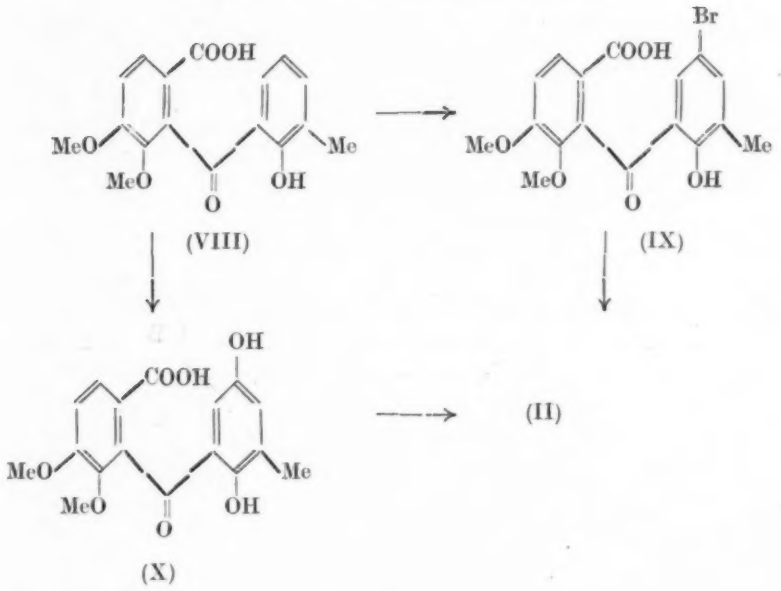
Among the natural polyhydroxy-2-methylanthraquinones, only a few possess more than four nuclear hydroxyl groups. These are dermocybin (Kögl and Postowsky, *Annalen*, 1925, **444**, 1), asperthecin (Howard and Raistrick, *Biochem. J.*, 1955, **59**, 475; Neelakantan *et al.*, *ibid.*, 1957, **66**, 234), and the anthraquinone pigments of *Cassia obtusifolia* (Takido, *Chem. Pharm. Bull.*, 1960, **8**, 246). 6-Hydroxycatenarin (I) has not so far been isolated

as a natural product, but its close structural relationship to catenarin (IV) would suggest the possibility of the former also occurring in nature. Hence this substance (I) has now been synthesised. 3,4,5-Trimethoxy-2-(2′-hydroxy-4′-methyl)benzoylbenzoic acid (V), obtained from 3,4,5-trimethoxyphthalic anhydride and *m*-cresol, has been subjected to *para* nuclear oxidation with alkaline potassium persulphate and the resulting quinol derivative (VI) cyclised with fuming sulphuric acid-boric acid mixture when the trimethyl ether (VII) is obtained. This on complete demthylation using hydrobromic acid and acetic acid gives 6-hydroxycatenarin* (I).



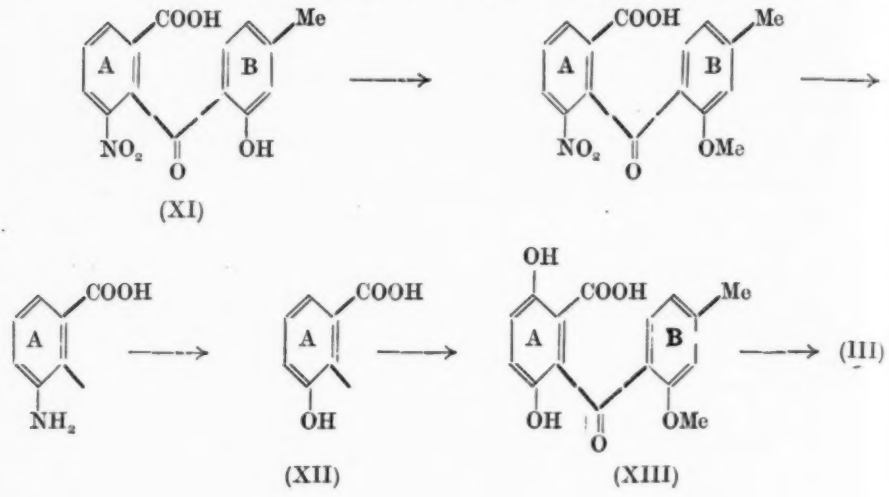
Gatenbeck (*Acta Chem. Scand.*, 1958, **12**, 1985; 1959, **13**, 705) recently isolated a compound, designated as 'compound A', from *Penicillium islandicum* and converted it into a polyhydroxyanthraquinone by treatment with concentrated sulphuric acid. This anthraquinone pigment was shown to be 1,4,7,8-tetrahydroxy-2-methylanthraquinone (II) by synthesis, using two different methods. In one, 3,4-dimethoxyphthalic anhydride was condensed with toluhydroquinone in presence of anhydrous aluminium chloride-sodium chloride melt. In the other, the above phthalic anhydride was condensed with *o*-cresol and the resulting 3,4-dimethoxy-2-(2′-hydroxy-3′-methyl)benzoylbenzoic acid (VIII) was monobrominated (IX) and cyclised to (II), the bromine atom being replaced by a hydroxyl group during this process; the yield, however, was very low by this method though it was less ambiguous as compared with the first method. In the present synthesis, the above benzoylbenzoic acid (VIII) has been subjected to oxidation with alkaline potassium persulphate and the quinol derivative (X) converted into the anthraquinone (II), using fuming sulphuric acid, in a fairly satisfactory yield.

*After the present paper had been written, we have come across a reference of Birkinshaw and Gourley (*Biochem. J.*, 1961, **79**, 3P) where this compound has also been reported briefly. Their general method of preparation of this substance is the same as ours.



Helminthosporin (III) was first isolated as a metabolic product of *Helminthosporium gramineum* by Charles *et al.* (*Biochem. J.*, 1933, **27**, 499) and subsequently from a number of other *Helminthosporia* (Raistrick *et al.*, *ibid.*, 1933, **27**, 1170; 1934, **28**, 559). It was, however, known earlier as a synthetic product first prepared by Graves and Adams (*J. Amer. Chem. Soc.*, 1923, **45**, 2439) who condensed 3,6-dimethoxyphthalic anhydride with *m*-cresol and cyclised and demethylated, in one step, the resulting benzoylbenzoic acid. Subsequently, Raistrick *et al.* (*J. Chem. Soc.*, 1933, 488) reported a synthesis of helminthosporin in better yields. In their method, the ring-closure was in a different way. They condensed 3-methoxy-5-methylphthalic anhydride with hydroquinone dimethyl ether and cyclised the intermediate benzoylbenzoic acid. The present synthesis was undertaken to provide an example of nuclear oxidation in the benzene ring in the left of the molecule (A); the earlier cases involved nuclear oxidation in the right half (B). 3-Nitro-2-(2′-hydroxy-4′-methyl)benzoylbenzoic acid (XI), obtained from 3-nitrophthalic anhydride and *m*-cresol, has been converted into 3-hydroxy-2-(2′-methoxy-4′-methyl)benzoylbenzoic acid (XII) by (*i*) methylation and hydrolysis of the resulting ether-ester, (*ii*) reduction of the nitro group to the amino, and (*iii*) conversion into the hydroxyl by diazotisation and hydrolysis. This benzoylbenzoic acid (XII) was oxidised with alkaline potassium persulphate to the quinol (XIII) and cyclised with fuming sulphuric acid to helminthosporin (III).

In the present synthesis, the feasibility of the nuclear oxidation in the left ring (A) of the benzoylbenzoic acid has been established. The overall yield is, however, poor (about 4%). The earlier synthesis by Graves and Adams (*loc. cit.*) had the same difficulty and the yield-reducing step was the last one in which ring-closure involved an unreactive nuclear position. On the other hand, in the method of Raistrick *et al.* (*loc. cit.*), the ring-closure involved a reactive position and the yields were good.



EXPERIMENTAL

3, 4,5-*Trimethoxy*-2-(2′-*hydroxy*-4′-*methyl*)*benzoylbenzoic Acid* (V).—To 3,4,5-trimethoxyphthalic anhydride (10 g.), dissolved in dry and freshly distilled *m*-cresol (60 c.c.), anhydrous aluminium chloride (20 g.) was added in small lots. The mixture was kept overnight at room temperature, then heated at 70° for 6 hours with stirring and left overnight. Crushed ice and HCl (conc., 10 c.c.) were added to the reaction mixture to decompose the complex. The excess of *m*-cresol was steam distilled and the aqueous layer decanted. The brown residue was dissolved in 1*N*-NaOH (180 c.c.) and the alkaline solution saturated with carbon dioxide. The phthalein, which was obtained as a byproduct, was filtered and the filtrate acidified with ice-cold HCl (conc.). The benzoylbenzoic acid separating was filtered, washed with water, and crystallised from methanol in colorless needles, m.p. 200-201°, yield 3.5 g. (Found: C, 61.9; H, 5.3. $C_{18}H_{18}O_7$ requires C, 62.4; H, 5.2%). It gave a reddish brown colour with ethanolic ferric chloride and a red colour with cold H_2SO_4 (conc.), turning purple on warming. With aqueous sodium carbonate and sodium hydroxide it gave yellow solutions.

3, 4, 5-*Trimethoxy*-2-(2′,5′-*dihydroxy*-4′-*methyl*)*benzoylbenzoic Acid* (VI).—To a stirred solution of the above acid (V) (2 g.) in aqueous KOH (1.3 g./40 c.c.) was added a saturated aqueous solution of potassium persulphate (1.9 g.) in course of 2 hours. The stirring was continued for another hour and the solution left overnight. On working up by the usual method, the quinol derivative was obtained as a brown solid. It crystallised from aqueous ethanol as brown clusters of needles, m.p. 213-14°, yield 0.8 g. (Found: C, 59.4; H, 5.4. $C_{18}H_{18}O_8$ requires C, 59.7; H, 5.0%). It gave a green colour with ethanolic ferric chloride and a dark solution with cold H_2SO_4 (conc.), turning bluish violet on warming. With aqueous NaOH, it gave an orange solution.

1,4,5,6,7-*Pentahydroxy*-2-*methylanthraquinone* (6-*Hydroxycatenarin*) (I). *Step* 1.—The above quinol derivative (VI) (1.2 g.) was heated with a mixture of freshly melted and powdered boric acid (1.2 g.) and H_2SO_4 (conc., 20 c.c.). At 70°, fuming H_2SO_4 (20% SO_3)

(3. c.c.) was added and the mixture kept at this temperature for an hour. The deep reddish blue solution was then poured on crushed ice and stirred. After a few hours, the precipitate was coagulated by heating on a boiling water bath. The deep red solid was filtered and washed with hot water. After drying, it was once crystallised from dioxan, m.p. 239-41°, yield 1.0 g. Since partial demethylation seemed to have taken place during the ring-closure, the product was directly used for further stages.

Step 2.—The crude trimethyl ether (VII) (0.7 g.) was refluxed with a mixture of glacial acetic acid (70 c.c.) and HBr (constant boiling; 105 c.c.) for 20 hours. The solution was filtered hot and the filtrate cooled in ice when a red solid separated. It crystallised from dioxan as maroon-coloured needles, m.p. 283-85°. It sublimed under vacuum (2-3 mm; 200-210°) as a red solid, m.p. 285-86°. (Found: C, 59.2; H, 3.8. $C_{15}H_{10}O_7$ requires C, 59.6; H, 3.3%). It gave the following colour reactions: aqueous sodium carbonate—blue; aqueous NaOH—blue; H_2SO_4 (conc.)—blue in dilute solution and deep blue with a feeble dichroic violet in concentrated solution; methanolic magnesium acetate—pink. It is insoluble in aqueous sodium bicarbonate.

It had the following spectral absorptions: U.V., λ_{max}^{dioxan} 285 (log. ϵ 4.37) and 485mμ (log ϵ 4.11); I.R. (KBr disc): 3.00 (s), 4.25 (m), 6.05 (s), 6.30 (s), 7.05 (s), 7.35 (s), 7.60(s), 7.90 (s), 8.35 (s), 8.80 (s), 9.20 (w), 9.70 (m), 9.90 (m), 10.30 (w), 11.10 (w), 11.30 (w), 12.10 (m), 13.20 (w), 14.10 (m) μ.

On acetylation with acetic anhydride and H_2SO_4 (conc.) it gave a penta-acetate as pale yellow needles from ethyl acetate, m.p. 200-201°.

1,4,5,6,7-*Pentamethoxy-2-methylanthraquinone*.—The trimethyl ether (VII) was methylated by the dimethyl sulphate-acetone-potassium carbonate method; the pentamethyl ether crystallised from methanol as lemon-yellow needles, m.p. 158-59°. (Found: C, 64.0; H, 5.6. $C_{20}H_{20}O_7$ requires C, 64.5; H, 5.4%).

3,4-*Dimethoxy*-2-(2′,5′-*dihydroxy*-3′-*methyl*)*benzoylbenzoic Acid* (X).—3,4-Dimethoxy-2-(2′-hydroxy-3′-methyl)benzoylbenzoic acid (VIII) (Jacobson and Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 288) (2 g.) was dissolved in aqueous KOH (1.6. g./40 c.c.) and subjected to nuclear oxidation with potassium persulphate (2.4 g.) under the same conditions as in the earlier case. The quinol derivative was obtained as yellow prisms from methanol, m.p. 220-21°, yield 0.25 g. It underwent change on drying. (Found in an air-dried sample: C, 57.8; H, 5.5. $C_{17}H_{16}O_7,1H_2O$ requires C, 58.3; H, 5.1%). It gave a green colour with ethanolic ferric chloride and a dark red colour with H_2SO_4 (cold, conc.) turning deep purple on heating. With aqueous sodium carbonate and NaOH, it gave red solutions.

1,4,7,8-*Tetrahydroxy*-2-*methylanthraquinone* (II).—The above benzoylbenzoic acid (X) (0.2 g.) was heated with a mixture of melted boric acid (0.25 g.) and H_2SO_4 (conc., 15 c.c.) in an oil bath. At 100°, fuming H_2SO_4 (1. c.c.) was added and the mixture kept at this temperature for 3 hours and then for 1 hour at 150-60°. The purple solution was cooled and poured into crushed ice with stirring. The anthraquinone was isolated after coagulation on a boiling water bath. It was sublimed under vacuum (2-3 mm; 200-210°) and crystallised from toluene in red needles, m.p. 252-54°, yield, 0.05 g. Gatenbeck (*loc. cit.*) reported the m.p. as 255°. (Found: C, 62.4; H, 3.8. $C_{15}H_{10}O_6$ requires C, 62.9; H, 3.5%). It had the same properties as recorded for the substance obtained by Gatenbeck.

The tetrahydroxyanthraquinone was acetylated with acetic anhydride and H_2SO_4 (conc.); the tetra-acetate crystallised from glacial acetic acid as yellow needles, m.p. 206-208°. Gatenbeck (*loc. cit.*) recorded its m.p. as 208-10°. (Found: C, 60.3; H, 4.5. $C_{23}H_{18}O_{10}$ requires C, 60.8; H, 4.6%).

3-*Nitro*-2-(2′-*methoxy*-4′-*methyl*)*benzoylbenzoic Acid*.—3-Nitro-2-(2′-hydroxy-4′-methyl)benzoylbenzoic acid (XI) (Eder and Widmer, *Helv. Chim. Acta*, 1922, **5**, 3) was methylated with dimethyl sulphate and alkali according to the method of Stoll and Becker (*Rec. trav. chim.*, 1950, **60**, 553). In the work of the latter authors, they used the resulting ether-ester and carried out a number of steps and later hydrolysed the ester group. We have found it more convenient to hydrolyse the ester to the acid at this stage and to carry out the later steps in a simpler way. The ether-ester (36 g.) was hydrolysed with 10% KOH (100 c.c.) by heating till a clear solution was obtained. The benzoylbenzoic acid was isolated by acidification of the alkaline solution. It crystallised from glacial acetic acid as colorless needles, m.p. 194-95°, yield, 31 g. (Found: C, 60.6; H, 4.5. $C_{16}H_{13}O_6N$ requires C, 61.0; H, 4.1%). It dissolved in aqueous sodium bicarbonate giving a colorless solution. It gave no colour with ethanolic ferric chloride but a lemon-yellow solution, turning red on warming, with H_2SO_4 (conc.).

3-*Amino*-2-(2′-*methoxy*-4′-*methyl*)*benzoylbenzoic Acid*.—To freshly prepared ferrous hydroxide, obtained from a solution of ferrous sulphate (25 g./150 c.c.) and ammonia (conc., 40 c.c.), was added a hot solution of the above nitro compound (3.1 g.) in 10% ammonia (200 c.c.). The mixture turned brown and was heated for 20 minutes and filtered. The residue was washed twice with hot 10% ammonia. The combined filtrate was boiled free of the ammonia, filtered, and the amino compound precipitated from the hot filtrate by the addition of potash alum (3.5 g.). It crystallised from ethanol as colorless plates, m.p. 197-98°, yield 2g. Mixed m.p. with the nitro compound was depressed (170-75°). (Found: C, 66.9; H, 5.7. $C_{16}H_{15}O_4N$ requires C, 67.4; H, 5.3%). It dissolved in alkalies to form yellow solutions and gave an orange solution, changing to red on warming, with H_2SO_4 (conc.).

3-*Hydroxy*-2-(2′-*methoxy*-4′-*methyl*)*benzoylbenzoic Acid* (XII).—The above amino compound (2.3 g.) was dissolved in a small quantity of ammonium hydroxide and acidified with HCl (dil.). It separated as a milky precipitate which dissolved in excess of 5% HCl. The solution of the hydrochloride was cooled to 0° and an aqueous solution of sodium nitrite (0.79 g.) added dropwise with vigorous stirring. After the addition was over, the mixture was boiled for ½ hour. On cooling, the hydroxy-acid separated. It crystallised from aqueous ethanol as light yellow prisms, m.p. 190-91°, yield 1.26 g. Stoll and Becker (*loc. cit.*) reported the m.p. as 189-90°. It gave a reddish brown colour with ethanolic ferric chloride.

3,6-*Dihydroxy*-2-(2′-*methoxy*-4′-*methyl*)*benzoylbenzoic Acid* (XIII).—The above hydroxy-benzoylbenzoic acid (XII) (2.0 g.) was subjected to nuclear oxidation using a saturated aqueous solution of potassium persulphate (2.4 g.) and aqueous KOH (1.6 g./40 c.c.) as in earlier cases. The quinol derivative crystallised from aqueous ethanol as light brown needles, m.p. 108-109° (decomp.), yield 0.2 g. (Found: C, 63.5; H, 4.8. $C_{16}H_{14}O_6$ requires C, 63.6; H, 4.6%). It gave a green colour with ethanolic ferric chloride and dissolved in alkalies to form violet solutions. With H_2SO_4 (cold, conc.), it gave a brown-red solution, turning dark violet on warming.

4,5,8-*Trihydroxy*-2-*methylanthraquinone* (*Helminthosporin*) (III).—The above benzoylbenzoic acid (XIII) (0.9 g.) was cyclised and simultaneously demethylated using sulphuric acid-boric acid mixture as in the earlier case. The anthraquinone crystallised from pyridine as flat, maroon needles with a bronze lustre, m.p. 226-27°, yield, 0.04 g. (Found: C, 66.7; H, 4.6. $C_{15}H_{10}O_5$ requires C, 66.7; H, 3.7%). It was identical with a sample of natural helminthosporin. λ_{max}^{MeOH} (log ϵ) for synthetic helminthosporin: 231 (4.52), 253 (4.15), 287 (3.80), 320 (2.91) and 490 mμ (4.10); for natural helminthosporin: 230 (4.64), 254 (4.30), 287 (3.93), 320 (2.96) and 490 mμ (4.09).

Its triacetate was prepared using acetic anhydride and sulphuric acid (conc.) and it crystallised from a mixture of glacial acetic acid and acetic anhydride as pale yellow needles, m.p. 223-24°, agreeing with the earlier record (Raistrick *et al.*, *loc. cit.*).

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CHEMISTRY DEPARTMENT,
UNIVERSITY OF DELHI,
DELHI-6.

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Synthesis of 2′-Hydroxy-7,4′-dimethoxyisoflavone

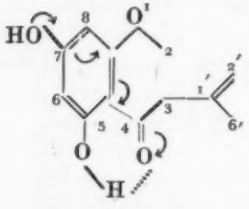
K. Aghoramurthy, A. S. Kukla, and T. R. Seshadri

2′-Hydroxy-7,4′-dimethoxyisoflavone has been prepared both by partial methylation of 7,2′,4′-trihydroxyisoflavone and by partial demethylation of the trimethoxy compound. Its constitution is established by ethylation and independent synthesis of the ethyl ether.

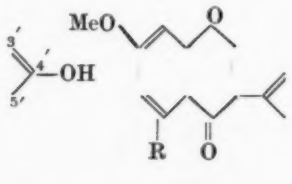
In natural products, 2′-hydroxyisoflavonoids are far more common than similarly substituted flavonoids. These were known earlier as component units in rotenoids. The synthesis of rotenoids based on this consideration has been pursued in this laboratory (Seshadri *et al.*, *Proc. Ind. Acad. Sci.*, 1953, **37A,** 791; 1955, **42A,** 36, 192; 1958, **47A,** 292; *J. Sci. Ind. Res.*, 1960, **19B,** 76). Munduserone (Finch and Ollis, *Proc. Chem. Soc.*, 1960, 176, 177), recently discovered, is a simpler member of this type. Certain isoflavone derivatives, like pterocarpin and homopterocarpin, also have this unit and recently the synthesis of homopterocarpin has been carried out by following this idea (Aghoramurthy *et al.*, *Curr. Sci.*, 1961, **30,** 218). Several 3-phenylcoumarin derivatives (wedelolactone type) that have been recently discovered have also a condensed furan ring. These are based on the 2′-hydroxy-3-phenylcoumarin system, which is very closely analogous to the corresponding isoflavone structure. Their synthesis has also been based on the initial formation of the 2′-hydroxy compounds.

In the synthesis of the complex molecules, mentioned above, there is need for the preparation of isoflavones with the 2′-hydroxyl free and the others methylated. Success has now been achieved in this work both by partial methylation of polyhydroxy-isoflavones and by partial demethylation of their full methyl ethers. As a typical example, the preparation of 7, 4′-dimethoxy-2′-hydroxyisoflavone (IV) is described in this paper.

Hydroxy-isoflavones can be partially methylated or demethylated based on the difference in reactivity of the various hydroxyl groups. Thus a hydroxyl at the 7-position is rendered more reactive by electromeric polarization arising from the carbonyl (I). This carbonyl further deactivates the hydroxyl in 5-position by chelation. Apparently hydroxyls in the side phenyl do not seem to be affected by this influence.



(I)



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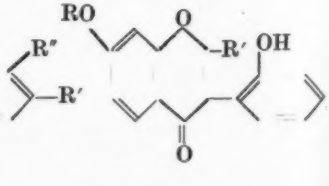


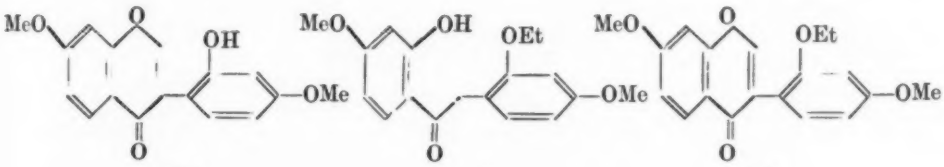
(III)

(a): R″ = H; R = R′ = OH.
(b): R = R″ = H; R′ = OH.
(c): R = R′ = R″ = OH.
(d): R = R″ = OH; R′ = OMe.

(a): R = R′ = Me.
(b): R = Me; R′ = H.
(c): R = H; R′ = Me.
(d): R = R′ = H.

Using this property prunetin (IIa), isoformononetin (IIb), and santal (IIc) have been conveniently prepared by partial methylation of the corresponding hydroxy-isoflavones (Seshadri *et al.*, *Proc. Ind. Acad. Sci.*, 1950, **32A,** 256; 1951, **33A,** 257; 1953, **37A,** 531). 7-Methoxy-2′-hydroxy-2-methylisoflavone(IIIa) and 7-methoxy-2′-hydroxyisoflavone (IIIb) were obtained respectively by partial methylation of 7, 2′-dihydroxy-2-methylisoflavone (IIIc) (Seshadri and Varadarajan, *ibid.*, 1953, **37A,** 384) and 7,2′-dihydroxyisoflavone (IIId) (Grover and Seshadri, *ibid.*, 1953, **38A,** 122). In the last two cases partial methyl ethers were obtained in good yields even when a large excess of methyl iodide was used. The reason for the unusual resistance of the 2′-hydroxyl to methylation is not yet clear.

Dhar *et al.* (*J. Sci. Ind. Res.*, 1956, **15B,** 285) studied the relative reactivities of 3′- and 4′-hydroxyls and found the latter to be more reactive. Santal-4-methyl ether (IId) was prepared in this way by partial methylation of santal. Its constitution was proved by the usual ethylation technique.



(IV) (V) (VI)

During partial methylation of 7, 2′, 4′-trihydroxyisoflavone it is now found that its 7-methyl ether can be conveniently prepared using one mole of dimethyl sulphate. Further methylation with one mole of dimethyl sulphate gives mainly 7, 4′-dimethoxy-2′-hydroxyisoflavone. The constitution of the product was proved by its ethylation to afford 7, 4′-dimethoxy-2′-ethoxyisoflavone (VI), which agreed both in m.p. and U.V. absorption with an authentic sample, prepared by direct synthesis starting from 2-ethoxy-4-methoxyacetophenone and passing through the following stages: (1) 2-ethoxy-4-methoxyphenylacetic acid (Willgerodt reaction), (2) the corresponding amide and nitrile, (3) 2-hydroxy-4-methoxyphenyl-2-ethoxy-4-methoxybenzyl ketone (V), (4) the isoflavone (VI).

Demethylation of 7, 2′, 4′-trimethoxyisoflavone with aluminium chloride in various solvents have been studied. The use of benzene gives mainly 7,2′4′-trihydroxyisoflavone, but demethylation in nitrobenzene solution provides a mixture of 7,4′-dimethoxy-2′-hydroxyisoflavone(IV) and 7-methoxy-2′,4′-dihydroxyisoflavone. When acetonitrile is used as a solvent, only the former isoflavone (IV) is obtained in about 70% yield. This seems to be a very convenient method for partial demethylation of the 2′-methoxyl group and is the first example of partial demethylation in the side phenyl nucleus of isoflavones. Its use is being extended for the synthesis of naturally occurring isoflavonoids and related compounds.

EXPERIMENTAL

7, 2′, 4′-*Trihydroxyisoflavone*.—A solution of 7, 2′, 4′-trimethoxyisoflavone (1.4 g.) (Späth *et al.*, *Ber.*, 1940, **73B,** 1) in dry benzene (50 c.c.) was refluxed with anhydrous alu-

minium chloride (4 g.) for 6 hrs. on a steam bath. The benzene was distilled and the residue decomposed with ice and HCl. The solid obtained was macerated with aqueous sodium carbonate(5%). The carbonate solution furnished on acidification the desired isoflavone which crystallised from aqueous acetone as almost colorless needles (1 g.), m. p. 284° with darkening. (Found: C, 66.8; H, 4.3. $C_{15}H_{10}O_5$ requires C, 66.7; H, 3.7%).

7-*Methoxy*-2′,4′-*dihydroxyisoflavone*.—A mixture of the above isoflavone (1.2 g.), dimethyl sulphate (0.42 c.c.), potassium carbonate (4 g.), and dry acetone (300 c.c.) was refluxed for 4 hrs. on a water bath. Potassium salts were filtered, washed with dry acetone, and the combined acetone extract was evaporated. The residue was macerated with aqueous sodium carbonate (5%) to remove the unchanged trihydroxyisoflavone. 7-Methoxy-2′,4′-dihydroxyisoflavone (1 g.) crystallised from ethanol as colorless needles, m.p. 212°. (Found: C, 67.8; H, 4.4. $C_{16}H_{12}O_5$ requires C, 67.6; H, 4.2%).

7, 4′-*Dimethoxy*-2′-*hydroxyisoflavone* (IV).—The preceding isoflavone (500 mg.), dimethyl sulphate (0.16 c.c.), potassium carbonate (2 g.), and dry acetone (150 c.c.) were refluxed for 3 hrs. on a water bath. Potassium salts were filtered, washed with dry acetone, and the combined acetone extract was distilled to remove the acetone. The residue was taken in ether and the ethereal solution extracted with aqueous NaOH (2%).

The ether solution was dried over ignited sodium sulphate and then the ether distilled. Trimethoxy-isoflavone (70 mg.) crystallised from benzene as colorless prisms, m.p. 148°.

The alkali-soluble portion was acidified, the solid filtered, and after drying was extracted in a Soxhlet with ethyl acetate. 7,4′-Dimethoxy-2′-hydroxyisoflavone (280 mg.) crystallised as needles in the receiver when the extract was cooled, m.p. 183-84°. It gave no colour with ethanolic ferric chloride. It is soluble in 2% alkali. (Found: C, 68.2; H, 4.9. $C_{17}H_{14}O_5$ requires C, 68.4; H,4.7%). The *acetate*, prepared by refluxing the isoflavone with acetic anhydride and fused sodium acetate for 1 hr., crystallised from dilute acetic acid as long colorless needles, m.p. 143°. (Found: C, 67.2; H, 5.0. $C_{19}H_{16}O_6$ requires C, 67.3; H, 4.7%).

The residue in the thimble of the Soxhlet after two crystallisations from ethanol separated as colorless needles, m.p. 212°, which was shown to be 7-methoxy-2′, 4′-dihydroxyisoflavone by comparison and mixed m.p.

7,4′-*Dimethoxy*-2′-*ethoxyisoflavone* (VI).—The isoflavone (IV) (0.2 g.), diethyl sulphate (0.13 c.c.), potassium carbonate (1 g.), and dry acetone (75 c.c.) were refluxed for 6 hrs. on a water bath. The product was macerated with aqueous NaOH (5%) and filtered. The insoluble 7,4′-*dimethoxy*-2′-*ethoxyisoflavone* (0.2 g.) crystallised from benzene-light petroleum (60-80°) as clusters of tiny needles, m.p. 132°. (Found: C, 69.9; H, 5.4. $C_{19}H_{18}O_5$ requires C, 69.9; H, 5.5%). U.V. absorption in methanol showed maxima at 240 and 287 mμ. A mixed m.p. with an authentic sample synthesised, as described later, showed no depression.

Partial Demethylation of 7,2′,4′-Trimethoxyisoflavone

Using Aluminium Chloride-acetonitrile.—7,2′,4′-Trimethoxyisoflavone (2 g.), anhydrous aluminium chloride (6 g.), and dry acetonitrile (50 c.c.) were refluxed for 6 hrs. on a steam bath. Acetonitrile was distilled and ice and HCl were added to decompose the

complex. The product was macerated with aqueous NaOH (2%) and filtered to remove the insoluble material which was found to be unchanged isoflavone. Alkaline extract on acidification gave 7, 4′-dimethoxy-2′-hydroxyisoflavone which crystallised as colorless needles (1.4 g.) form ethyl acetate, m.p. 183-84°. Mixed m.p. with the earlier sample of 7,4′-dimethoxy-2′ hydroxyisoflavone obtained by the partial methylation of 7-methoxy-2′, 4′-dihydroxyisoflavone was undepressed.

Methylation of the above isoflavone using dimethyl sulphate and acetone-potassium carbonate yielded 7,2′,4′-trimethoxyisoflavone, m.p. 148°, whereas ethylation using diethyl sulphate and acetone-potassium carbonate gave 7,4′-dimethoxy-2′-ethoxyisoflavone, m.p. 132°.

Using Aluminium Chloride-nitrobenzene.—A solution of aluminium chloride (3 g.) and 7, 2′, 4′-trimethoxyisoflavone (1 g.) in nitrobenzene (10 c.c.) was heated on a steam bath for 3 hrs. The mixture was decomposed with ice and HCl. The product was taken up in ether and extracted with 5% aqueous NaOH (2×20 c.c.). The alkaline extract was acidified and the product crystallised from a large volume of hot ethyl acetate when 7-methoxy-2′,4′-dihydroxyisoflavone crystallised as needles (0.5g.), m.p. 212° The mother liquors on further concentration gave 7, 4′-dimethoxy-2′-hydroxyisoflavone (0.2g.) which after one more crystallisation from ethyl acetate gave needles, m.p. 183-84°.

2-Ethoxy-4-methoxyphenylacetic Acid.—2-Ethoxy-4-methoxyacetophenone (34 g.), morpholine (33 c.c.) and sulphur (12 g.) were heated under reflux for 11 hrs. Excess of morpholine was removed from the chloroform solution of the product with dilute hydrochloric acid and the crude morpholide was refluxed for 11 hrs. with NaOH (105 g.) in water (800 c.c.), cooled, and filtered through a bed of hyflo-super-cel; the filtrate was acidified with HCl. The precipitated acid containing sulphur was macerated with aqueous sodium hydrogen carbonate, filtered, and acidified when the product separated as a brown solid (20 g.). Crystallisation from benzene-light petroleum (60-80°) gave the acid as colorless needles, m.p. 112-13°. (Found: C, 62.7; H, 6.9. $C_{11}H_{14}O_4$ requires C, 62.8; H, 6.7%).

2-Ethoxy-4-methoxyphenylacetamide.—A solution of the acid (5.5 g.) in chloroform (44 c.c.) containing PCl_3 (7.7 c.c.) was kept at room temperature for 2 hrs. and then warmed to 60° for 1 min. The clear solution was decanted and chloroform was removed under reduced pressure when the acid chloride was obtained as a pale brown oil. This acid chloride was gradually added in the course of 15 to 20 mins. with constant stirring to ice-cold liquor ammonia (25 c.c.). The solid separating was crystallised from hot water when the amide was obtained as colorless plates (4 g.), m.p. 131°. (Found: C, 63.1; H, 7.2. $C_{11}H_{15}O_3N$ requires C, 63.1; H, 7.2%).

2-Ethoxy-4-methoxyphenylacetonitrile.—The preceding dry amide (4 g.) was mixed with P_2O_5 (8 g.) and the mixture was gently distilled under reduced pressure when the nitrile passed over as a liquid which quickly solidified (1.9 g.). It crystallised from benzene-light petroleum (60-80°) as colorless, elongated prisms, m.p. 49-50°. (Found: C, 68.9; H, 7.3. $C_{11}H_{13}O_2N$ requires C, 69.1; H, 6.8%).

2,4-Dihydroxyphenyl-2-ethoxy-4-methoxybenzyl Ketone.—The above nitrile (1.8 g.) and dry resorcinol (3.5 g.) were dissolved in dry ether and fused zinc chloride (1.5 g.) was added. The mixture was saturated with dry HCl gas for 4 hrs. and kept at 0° in an ice-box for 3 days. Ether layer was removed and the solid ketimine hydrochloride washed with dry ether and

then hydrolysed by heating with water (75 c.c.) on a water bath for 6 hrs. The resulting solid was crystallised from dilute ethanol when the desired ketone (0.6 g.) was obtained as colorless needles, m.p. 120-21°. (Found: C, 67.4; H, 6.1. $C_{17}H_{18}O_5$ requires C, 67.5; H, 6.0%).

2-Hydroxy-4-methoxyphenyl-2-ethoxy-4-methoxybenzyl Ketone (V).—A solution of the above ketone (0.5 g.) in dry acetone (30 c.c.), dimethyl sulphate (0.17 c.c.) and ignited potassium carbonate (1 g.) were refluxed on a water bath for 6 hrs. The potassium salts were filtered, washed with dry acetone, and the combined acetone extract was evaporated. The residue was mecerated with aqueous sodium carbonate (5%) to remove any dihydroxyketone and then crystallised from ethanol when the *ketone* (0.45 g.) was obtained as colorless prisms, m.p. 106°. (Found: C, 67.8; H, 6.5. $C_{18}H_{20}O_5$ requires C, 68.3; H, 6.3%).

7,4′-Dimethoxy-2′-ethoxyisoflavone (VI).—A solution of the ketone (V) (0.4 g.) in dry ethyl formate (10 c.c.) was added in small portions to powdered sodium (0.4 g.) at 0°, the mixture being stirred continuously. It was stirred further for another 6 hrs. and then kept at 0° for 48 hrs. Ice-water and dilute HCl were added. The product was taken in glacial acetic acid (8 c.c.), refluxed for ½ hr., and diluted with water to obtain the ethoxyisoflavone (VI) (0.2 g.). It crystallised from benzene-light petroleum (60-80°) as colorless, small needles, m.p. 132°, undepressed by a sample described previously.

Department of Chemistry,
University of Delhi,
Delhi-6

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Synthesis of Thiazoline Compounds and their Mercurated Derivatives. Part II

B. B. Raul and G. N. Mahapatra

Action of *sym.*-di-(*p*-tolyl)thiourea on various ketones and their derivatives has been studied in presence of iodine and the resulting thiazoline compounds have been mercurated. The position of the acetoxymercuri group in the molecule has been ascertained. These thiazoline compounds have been converted into their corresponding thiazolone derivatives. The fungicidal and bactericidal actions of these compounds have also been investigated.

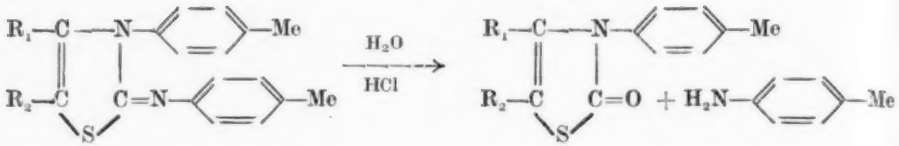
Action of thiocarbanilide on monochloroacetic acid (Lange, *Ber.*, 1879, **12,** 595; Desai *et al.*, *Rec. trav. chim.*, 1935, **54,** 118; Klare *et al.*, *J. Amer. Chem. Soc.*, 1930, **52,** 2137) and action of *sym.*-dialkylthiourea on α-haloketones have been studied (Garreau, *Compt. rend.*, 1953, **236,** 1575) and the respective formation of thiazolidone and thiazoline compounds has been reported.

Twelve ketones (both saturated and unsaturated alkyl and aralkyl) including one ketonic ester have been condensed with *sym.*-di-*p*-tolylthiourea in presence of iodine. From the mechanism of the action of haloketones on *sym.*-dialkylthiourea (Garreau, *loc. cit.*) and the action of thiourea and phenylthiourea on ketones and iodine (Mahapatra, this *Journal*, 1956, **33,** 527), the following possibility of the reaction between the components resulting in the formation of 2-(*p*-tolylimino)-3-(*p*-tolyl)-4-or 4,5-di-substituted thiazoline compound has been suggested (Mahapatra, *Proc. Indian Sci. Cong.*, 1957, Part III, 139).

Formation of the thiazoline derivative has been confirmed as follows. When *p*-bromophenacyl bromide was condensed with *sym.*-di-*p*-tolylthiourea in presence of ethanol, 2-(*p*-tolylimino)-3-((*p*-tolyl)-4-(*p*-bromophenyl)thiazoline (m.p. 85°; found S, 7.1; Br, 17.81. Calc. S, 7.35; Br, 18.39%) was formed which was identical in all physical and chemical properties to the compound prepared by condensing *p*-bromoacetophenone with *sym.*-di-(*p*-tolyl)thiourea in presence of iodine.

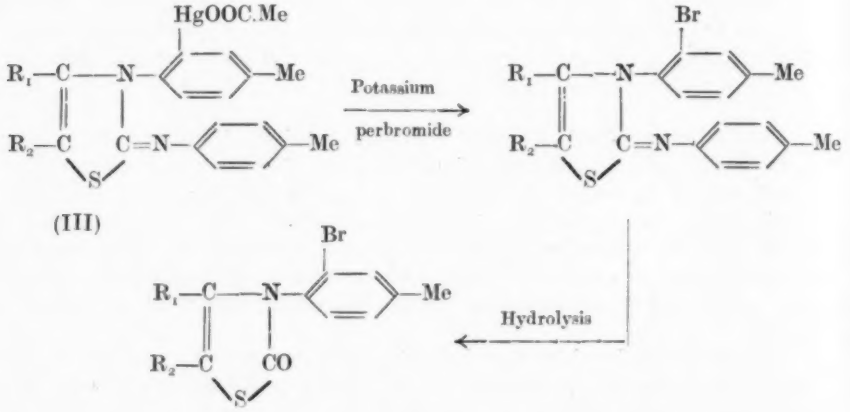
In the case of unsaturated ketones, like mesityl oxide, the reaction takes the above course, but in the ultimate product no unsaturation remains. The reason for this has been suggested earlier (Mahapatra, *loc. cit.*, 1956).

Presence of the imino group at C_2 is confirmed by the fact that when the compound is hydrolysed with HCl, a thiazolone derivative having a keto group at C_2 results along with *p*-toluidine as the clevage product. Presence of *p*-toluidine is detected by diazotisation of the filtrate and subsequent coupling with β-naphthol, when a red azo dye separates (m.p. 129°),



(I) (II)

These 2-*p*-tolylimino-3-*p*-tolylthiazoline compounds have been mercurated with one equivalent of mercuric acetate and the mercuric compounds so obtained are found to have only one acetoxymercuri group in the *p*-tolyl nucleus attached to the nitrogen at 3-position. The position of the acetoxymercuri group in the *p*-tolyl nucleus in the *o*-position to the nitrogen atom is justified from the earlier observations of mercuration of 2-arylimino-4-thiazolidones (Mahapatra and Rout, this *Journal*, 1955, **32**, 715). The possibility of the acetoxymercuri group entering the *p*-tolyl nucleus, attached to the imino group at C_2 of the thiazoline nucleus, is discarded on the ground that when the mercurated compounds are treated with potassium perbromide solution, monobromo derivatives having the bromine atom attached to the place previously linked to the mercury group are obtained.



These monobromo derivatives on hydrolysis yielded products which were not free from bromine and on analysis found to contain one equivalent of bromine. This indirectly suggests the linking of bromine atom to the *p*-tolyl nucleus attached to the nitrogen atom at 3-position, as shown above. If the bromine atom would have been linked to the *p*-tolyl nucleus attached to the imino group at C_2 position, the bromo compound on hydrolysis would not have retained the bromine atom, which is not the case. This finally confirms the position of the bromine atom and hence the position of the acetoxymercuri group in the *p*-tolyl nucleus attached to the nitrogen atom at 3-position.

Each of the thiazoline compounds, so obtained, has been hydrolysed with HCl in ethanol medium to afford the corresponding 3-*p*-tolyl-4- or 4,5-dialkyl-substituted 2-thiazolone.

The mercurated and some of the non-mercurated derivatives have been assayed for their fungicidal and bactericidal properties (Table II).

TABLE I

No.	Nature of R_1.	Nature of R_2.	Thiazoline derivatives (I). M.P.	Yield.	%Sulphur. Found.	Calc.	Thiazolone derivatives (II). M.P.	Yield.	% Nitrogen. Found.	Calc.
1.	Me	H	93°	85%	10.20	10.88	73°	56%	6.34	6.83
2.	Ph	H	118°	75	9.58	8.99	112°	75	5.50	5.24
3.	Me	Me	75°	70	10.34	10.39	62°	72	6.41	6.39
4.	Me_2CH-	H	65°	80	10.04	9.94	72°	56	5.75	6.00
5.	(*o*)OH-C_6H_4-	H	83°	63	9.21	8.60	90°	68	5.15	4.94
6.	Me	Bu	62°	73	9.89	9.14	58°	43	6.20	5.36
7.	Me_2CH-CH_2-	H	63°	67	9.55	9.52	70°	62	5.92	5.66
8.	Me	Et	62°	65	19.38	9.94	72°	63	6.13	6.00
9.	(*p*) Br-C_6H_4-	H	83°	72	6.98	7.35	65°	40	4.72	4.04
10.	(*p*)Cl-C_6H_4-	H	69°	76	7.80	8.19	62°	45	4.52	4.64
11.	Ph-CH_2CH_2-	H	93°	85	8.50	8.33	75°	60	4.92	4.74
12.	Me	C_2H_5OOC-	65°	63	8.92	8.74	76°	62	5.20	5.05

TABLE II

No. of comps.	M.P.	Acetoxymercuri derivatives (III). %Yield.	% Mercury. Found.	Calc.
1.	165°	58	35.80	36.23
2.	175°	82	32.40	32.57
3.	190°	80	35.54	35.33
4.	215°	82	34.23	34.48
5.	162°	85	32.02	31.74
6.	168°	70	33.21	32.89
7.	194°	75	34.25	33.67
8.	200°	67	34.28	34.48
9.	202°	78	29.20	28.86
10.	159°	62	30.98	30.84
11.	165°	90	31.50	31.15
12.	220°	85	32.35	32.05

N.B. Nature of R_1 and R_2 is the same as in Table I.

EXPERIMENTAL

2-(p-*Tolylimino*)-3-p-*tolyl*-4-*methylthiazoline*(I).—A mixture of *sym.*-di-(*p*-tolyl) thiourea (5.3g.), acetone (1g.), iodine (5g.), and dry benzene (30 c.c.) was refluxed on a water bath for 24 hours and for 6 to 8 hours without the use of condenser after distilling the benzene. The reaction product was kept in contact with ether for 48 hours with occasional stirring with a view to removing the unchanged ketone and iodine, presence of which made the product gummy. After decanting the ether, the crude product was boiled with water (50 c.c.). The water was decanted and the product treated with ammonia (*d* 0.888) to liberate the base. Some of the compounds remained gummy even after treatment with ammonia, but these could be made solid by occasionally scratching the product, keeping it for a

longer time in ammonia (conc.). The product was finally crystallised from EtOH-AcOH, m.p. 93°, yield 85%. (Found: N, 9.11; S,10.2. $C_{18}H_{13}N_2S$ requires N, 9.52; S,10.88%).

Mercuration of (I).—The preceding thiazoline (1.7 g.), dissolved in EtOH-AcOH (50:50), was treated with an ethanolic solution of mercuric acetate (2 g. in 30 c.c. of ethanol, acidified with acetic acid). The mixture was stirred with a glass rod and kept for 24 hours till the precipitate appeared. In some cases the precipitate appeared after adding a small amount of water to the mixture. The residue was then collected by filtration, washed thoroughly with hot water, and finally with ethanol and very dilute acetic acid, m.p. 165°, yield 58%. (Found: Hg, 35.80. $C_{20}H_{20}O_2N_2SHg$ requires Hg, 36.23%).

TABLE III

Bactericidal and fungicidal data of mercurated and non-mercurated thiazoline derivatives.

*No.	Bactericidal activity.		Fungicidal activity (% germinations in 10 p.p.m).	%Germination in the control.	Unmercurated compounds.		
	E. coli.	*S.A.*			Bac. activity. *S.A.*	*E. coli.*	% Germination at 10 p.p.m.
1.	1 : 10,000	1 : 10,000	-	-			-
2.	1 : 10,000	1 : 50,000	25	25			-
3.	1 : 20,000	1 : 100,000	37	90			-
4.	1 : 10,000	1 : 20,000	..	..			-
5.	1 : 50,000	1 : 50,000	..	..			-
6.	1 : 20,000	1 : 100,000	..	..			-
7.	1 : 50,000	1 : 20,000	..	..			-
8.	1 : 50,000	1 : 10,000	..	..			-
9.	1 : 50,000	1 : 100,000	20	65			
10.	1 : 100,000	1 : 100,000	20	85	1 : 1000	1 : 1000	70
11.	1 : 50,000	1 : 50,000	37	80			-
12.	1 : 50,000	1 : 100,000	16	90	1 : 1000	1 : 1000	80

* The compounds refer to those in Table I.

3-p-*Tolyl*-4-*methyl*-2-*thiazolone* (II).—The thiazoline (1g.) was taken in a conical flask. To this rectified spirit (30 c.c.) and HCl (conc., 4 c.c.) were added. The mixture was refluxed for 4 hours, the excess ethanol was distilled, water was added into the flask, and made just alkaline. The resulting precipitate was collected by filtration and recrystallised from ethanol, m.p. 73°, yield 56%. (Found: N, 6.34; S, 15.13. $C_{11}H_{11}ONS$ requires N, 6.83; S, 15.61%).

CHEMISTRY DEPARTMENT,
RAVENSHAW COLLEGE,
CUTTACK,

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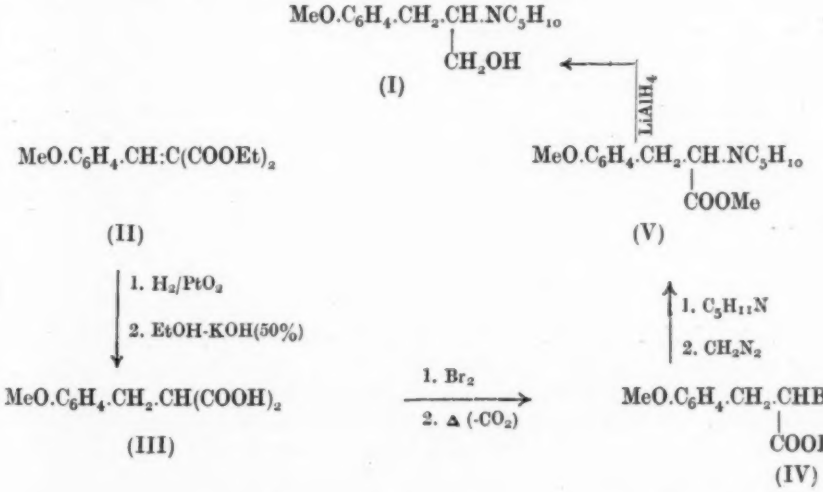
Synthesis of 3-Anisyl-2-piperidylpropanol[n]

S. C. Pakrashi and S. K. Roy

Synthesis of 3-anisyl-2-piperidylpropanol[n] (I), characterised through its hydrochloride, m.p. 212°, is described.

Alangine A, m. p. 85°, $[\alpha]_D$ -41.3° ($CHCl_3$), an alkaloid isolated from the root-bark of *Alangium lamarckii* Thw. (*Alangiaceae*), was proposed (Bhakuni *et al.*, *J. Sci. Ind. Res.*, 1960, **19B**, 8) to have the structure (I). Its possible identity with alangine, m.p. 80°, $[\alpha]_D$ -34° ($CHCl_3$), isolated from the same source (Chopra and Chowhan, *Indian J. Med. Res.*, 1934, **21**, 507), was also indicated. The arguments put forward in support of this structural assignment are not, however, very convincing. Since we have been actively interested in the field (Roy and Pakrashi, *Ann. Biochem. Exptl. Med.*, 1960, **20**, 103; Dutta and Pakrashi, *ibid.*, p. 279) for some time, we undertook and achieved the synthesis of (I) by the following route:



Anisylidenemalonic ester (II), prepared according to Knoevenagel (*Ber.*, 1898, **31**, 2594) was hydrogenated in ethanol over Adams' catalyst. Saponification of the product and purification by distillation and crystallisations from benzene afforded the corresponding saturated dicarboxylic acid (III) in flakes, m.p. 122° (uncorr.). Bromination of (III) followed by decarboxylation furnished 2-bromo-3-anisylpropionic acid (IV). The bromo-acid was condensed with piperidine, esterified, and reduced with $LiAlH_4$ to yield 3-anisyl-

2-piperidylpropanol[11] (I), isolated as hydrochloride in needles from acetone or benzene-methanol, m.p. 212° (uncorr.). The infrared absorption of the hydrochloride is reproduced in Fig. 1.

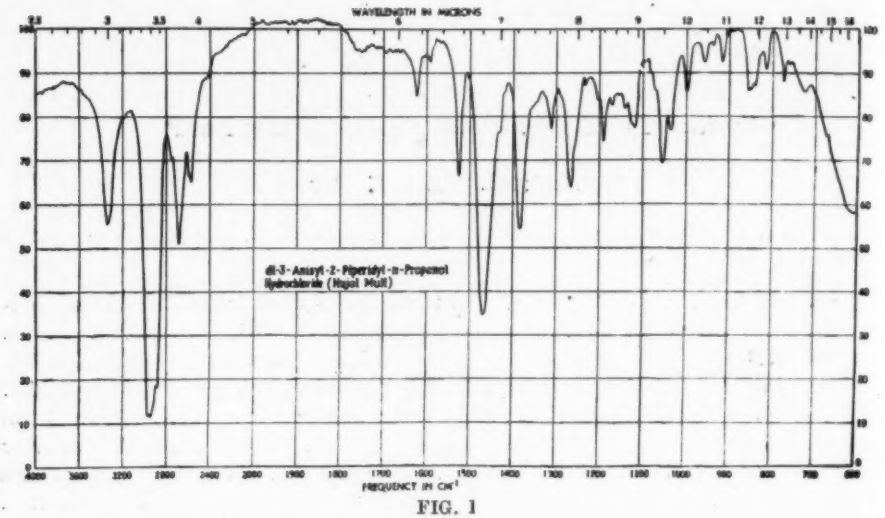


FIG. 1

After the completion of our work we came across the reported synthesis (Kapil *et al.*, *J. Sci. Ind. Res.*, 1961, **20B**, 136) of (I). The synthetic sample has been claimed to be different from alangine A without disclosing the mode of comparison. Any way, the above report necessitated the publication of the details of our work without having a chance to confirm the identity or non-identity of our compound with alangine A. Our method and data, however, differ from those of Kapil *et al.* (*loc. cit.*) in some important aspects (*vide* Experimental), the notable one being the melting point of the hydrochloride of the final product, which they report as 164°, whereas our sample melts at 212°.

EXPERIMENTAL*

Anisylidenemalonic Ester (II).—Freshly distilled anisaldehyde (40 g.) and malonic ester (49 g.) were mixed together with diethylamine (1 c.c.) and the mixture was left at room temperature for 10 days. The reaction mixture was heated on a water-bath for 6 hrs. and distilled. The fraction distilling at 206-208°/9 mm was collected; yield 26g. (32%).

Anisylmalonic Acid (III).—The preceding ester (II) (26 g.) was dissolved in ethanol, charcoaled, filtered directly in the reaction flask, and hydrogenated at ordinary pressure over Adams' catalyst (0.3 g.) (2.1 litres of hydrogen were taken up). The slurry was filtered, the filtrate freed of solvent, and distilled at 190-92°/9 mm; yield 25 g. (95.5%).

*All melting points are uncorrected. Analyses were done by Dr. A. Bernhardt, Max-Planck Institute, Mülheim (Ruhr), W. Germany and Drs. Weiler and Strauss, Oxford, England.

The total ester was added dropwise to a 50% ethanolic KOH (5 c.c.) and the solution was warmed on a water-bath for 4 hours, cooled, and poured in water (15 c.c.) containing crushed ice (15 g.). The solution was extracted with ether and the aqueous layer acidified with HCl (conc., *p*H 3-4) in suchwise that the temperature did not rise above 20°. The separated acid was extracted with ether, washed with water, dried (anhyd. Na_2SO_4), and concentrated. The oily residue on crystallisation from benzene afforded (III) in flakes, m.p. 122°, yield 16g. (80%). The aqueous portion was saturated with NaCl and extracted with ether; after the usual working up it gave a solid, m.p. 190-200°. It showed $FeCl_3$ coloration indicating that demethylation had occurred during strong alkaline hydrolysis. It was reconverted to the required anisylmalonic acid with Me_2SO_4 and KOH, the total yield of (III) being almost quantitative. (Found: C, 58.51; H, 5.46. Calc. for $C_{11}H_{12}O_5$: C, 58.93; H, 5.40%).

2-*Bromo*-3-*anisylpropionic Acid* (IV).—The dicarboxylic acid (III) (5.6 g.) was taken in dry ether and dry bromine (0.9 c.c, ~1.5*M*) was added dropwise with constant shaking till the solution became red-brown. It was left for ½ hr. and stirred occasionally (cf. Fischer, *Ber.*, 1904, **37,** 3064). The ethereal solution was washed, dried (anhyd. Na_2SO_4), and the solvent distilled. The resulting brownish yellow viscous liquid (7 g.) was heated at ordinary pressure at 150-60° for 4 hours in an oil bath. A portion of the gummy brown mass was sublimed at 80-90°/0.01 mm as a low-melting solid.

Methyl 3-*Anisyl*-2-*piperidylpropionate* (V).—Treatment of a solution of the bromo-acid (IV) (5 g.) in ether with piperidine (3 g.) in the same solvent resulted in an immediate separation of an oil. It was either left for 10 days when the oil solidified in needles or refluxed for 4 hours on a water bath. The product was directly methylated with diazomethane. The ester was taken up in 2*N*-HCl, basified, and extracted with $CHCl_3$ in the conventional way to yield 4.8 g. (92%) of the crude material.

3-*Anisyl*-2-*piperidylpropanol*[n] (I).—The ester (V) (2 g.) in dry ether (50 c.c.) was gradually added to a cooled and constantly stirred suspension of $LiAlH_4$ (6 g.) in ether (300 c.c.). The mixture was then refluxed for 4 hours on a water bath with stirring. The complex was decomposed with water and worked up to yield an oil (0.6 g., 26.5%). It was dissolved in ether (dry) with minimum amount of methanol and dry HCl gas was passed through the cooled solution. The hydrochloride was dissolved in hot water, treated with charcoal, and filtered. The filtrate was basified, extracted with ether, and the solvent removed. The base, thus obtained, was chromatographed over neutral alumina (E. Merck) in a column (12 × 1.4 cm) and eluted successively with petroleum ether, petroleum ether-benzene (1:1), benzene, and chloroform. Among the oily residues from the later fractions of benezene only those which responded to the alkaloidal tests were collected together, reconverted to hydrochloride, and crystallised from absolute ethanol-acetone in light colorless flakes (103 mg.), m.p. 200°. Recrystallisations from acetone and then from methanol-benzene yielded pure 3-anisyl-2-piperidylpropanol[n] hydrochloride in small needles. (Found: C, 62.66; H, 8.71; N, 4.53. Calc. for $C_{15}H_{24}O_2NCl$: C, 63.03; H, 8.47; N, 4.91%). U.V. spectra in 95% EtOH: λ_{max} 276 (log ϵ 3.22) and 283 mμ (log ϵ 3.17); infrared (nujol mull) bands at 3337, 1623, 1525, 1312, 1265, 1189, 1170 and 1140 (shoulder), 1116, 1054, 1035, 998, 955, 938 (shoulder), 916, 815, 774 besides a broad split band between 855 and 840 cm^{-1}.

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INDIAN INSTITUTE FOR BIOCHEMISTRY AND EXPERIMENTAL MEDICINE,
CALCUTTA-13.

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SHORT NOTES

Substituted 3-Aminobenzo/f/quinolines

A. K. Chatterjee

Chatterjee (*J. Org. Chem.*, 1960, **25**, 1050) reported preparation of a number of derivatives of 1-amino-3-methylbenzo/f/quinoline for trials against *E. histolytica*. The present communication deals with the preparation of some derivatives of 3-amino-1-methylbenzo/f/quinoline as potential amoebacides.

The compounds were prepared by the condensation of 3-chloro-1-methylbenzo/f/-quinoline with the appropriate amine in boiling amyl alcohol and characterised as salicylates.

The condensation of ethyl acetoacetate with 2-naphthylamine and subsequent cyclisation of the product in concentrated hydrochloric acid according to Albert *et al.* (*J. Chem. Soc.*, 1948, 1284) gave 3-hydroxy-1-methylbenzo/f/quinoline, which was converted into the 3-chloro derivative by treatment with phosphorus oxychloride.

General Method of Preparation

3-Chloro-1-methylbenzo/f/quinoline (0.01*M*) was dissolved in amyl^{n} alcohol (30 c.c.) by heating and a slight excess of the appropriate amine added. The mixture was boiled under reflux for 20 hours.

The hydrochloride of the base separated on cooling. It was filtered, washed with ether, and dissolved in boiling dilute acetic acid. The solution was made alkaline with aqueous NaOH when the base separated as a sticky solid, which quickly solidified. This was filtered, washed with water, dried, and dissolved in hot benzene. The small amount of insoluble matter was removed by filtration and the filtrate treated with a solution of salicylic acid in ether. In a few hours, the salicylate of the base separated which, after filtration and washing with ether, was purified by crystallising thrice from benzene. The compounds are listed in Table I.

TABLE I

Compound.	Formula.	M.P.	%Carbon.		%Hydrogen.	
			Found.	Calc.	Found.	Calc.
3-*p*-Chloroanilino-MQ	$C_{20}H_{15}N_2Cl,C_7H_6O_3$	213°	71.26	70.97	4.79	4.60
3-*m*-Chloroanilino-MQ	$C_{20}H_{15}N_2Cl,C_7H_6O_3$	195°	71.10	70.97	4.65	4.60
3-*p*-Bromoanilino-MQ	$C_{20}H_{15}N_2Br,C_7H_6O_3$	218°	64.97	64.67	4.33	4.19
3-*m*-Bromoanilino-MQ	$C_{20}H_{15}N_2Br,C_7H_6O_3$	196°	64.71	64.67	4.53	4.19
3-*m*-Iodoanilino-MQ	$C_{20}H_{15}N_2I,C_7H_6O_3$	196°	58.85	59.11	3.76	3.83
3-Anilino-MQ	$C_{20}H_{16}N_2,C_7H_6O_3$	220°	77.00	76.78	5.42	5.21
3-*p*-Toluidino-MQ	$C_{21}H_{18}N_2,C_7H_6O_3$	220°	77.06	77.06	5.27	5.50
3-*m*-Toluidino-MQ	$C_{21}H_{18}N_2,C_7H_6O_3$	192°	77.43	77.06	5.74	5.50
3-*p*-Anisidino-MQ	$C_{21}H_{18}N_2O,C_7H_6O_3$	199.5°	73.99	74.34	5.47	5.31

N.B. MQ stands for 1-methylbenzo/f/quinoline salicylate. $C_7H_6O_3$ = salicylic acid.

Department of Preventive Medicine,
Armed Forces Medical College,
Poona-1.

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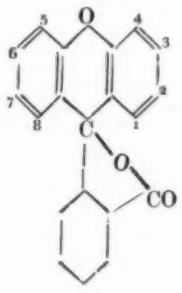
Evaluation of Fungicidal and Bactericidal Properties of Some Fluorans and Bromofluorans

(Miss) Kanti Srivastava and J. K. Mehrotra

The substituted fluorans and bromofluorans, recorded in Table I, were prepared by the method of Ghatak and Dutta (this *Journal*, 1926, **6**, 465). These have then tested for fungicidal activity on *Aspergillus niger*, using potato-glucose medium and for bacteriostatic activity on *S. aureus*, using nutrient broth medium containing beef extract and peptone, by dilution method. The medium (2 c.c.) was taken in each of the 10 test tubes and sterilised. To the first tube 2 c.c. of a solution of a compound containing 0.0256 g./10 c.c. was added. This mixture (2 c.c.) was withdrawn and added to the 2nd tube and the process continued to 9th tube. The 10th tube contained only the medium. The tubes were then inoculated with 24 hours' growth culture. The concentrations of the compounds in mg./c.c., at which there was complete inhibition, are recorded in Table I.

TABLE I

Fluoran =



No.	Compound.	Colour.	M.P.	Minimum conc. (mg./c.c.) at which complete inhibition takes place. *A. niger.*	*S. aureus.*
1.	4-Methyl-6-hydroxy-F	Light orange	115°	No inhibition	0.16
2.	3-Methyl-6-hydroxy-F	Chocolate	185°	Do	No inhibition
3.	2-Methyl-6-hydroxy-F	Do	175°	Do	0.32
4.	2-Chloro-6-hydroxy-F	Brownish yellow	190°	..	0.32
5.	1,3,6-Trihydroxy-F	Brown	175°	No inhibition	0.64
6.	2,6-Dihydroxy-F	Dark brown	182°	1.28	0.64

TABLE I (contd.)

No.	Compound.	Colour.	M. P.	Minimum conc. (mg./c.c.) at which complete inhibition takes place. *A. niger.*	*S. aureus.*
7.	4,5,7-Tribromo-6-hydroxy-F	Brown	205°	1.28	1.28
8.	4-Methyl-6-hydroxy-3,5,7-tribromo-F	Orange	248°	0.64	0.64
9.	2-Methyl-6-hydroxy-3,5,7-tribromo-F	Light orange	248°	0.16	0.32
10.	2-Chloro-5,7-dibromo-6-hydroxy-F	Reddish brown	200°	1.28	No inhibition
11.	4-Chloro-5,7-dibromo-6-hydroxy-F	Whitish orange	200° (decomp.)	0.64	0.64
12.	2,6-Dihydroxy-4,5-dibromo-F	Dirty yellow	180°	No inhibition	0.32
13.	1,3,6-Trihydroxy-4,5-dibromo-F	Dirty orange	218°	..	0.16

CHEMICAL LABORATORIES,
D. A. V. COLLEGE,
KANPUR.

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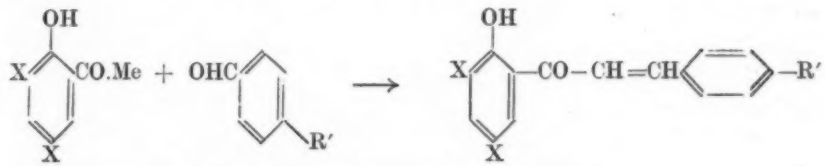
Chalkones as Bactericidal Compounds

S. S. Tiwari and A. Singh

Marrian *et al.* (*J. Chem. Soc.*, 1947, 1419) have prepared several aminochalkones on the basis that the grouping—C=C—CO—is present in many naturally occurring antibiotics, which may be responsible for the antibacterial activity. This type of grouping is also present in the chalkone. The bactericidal activity of chalkones has also been reported by Jeney *et al.* (*Zentrl. Bact. parasitenk Abt. I Org.*, 1955, **163,** 291 and Minorn *et al.* (*J. Agrl. Chem. Soc. Japan*, 1954, **28,** 791) that *o*-furfurylideneacetone and dibenzylidenediacetone are markedly toxic to rats. Keeping this in view, several chalkones have been prepared by condensing 2-hydroxy-3.5-dichloroacetophenone with benzaldehyde, *p*-nitro-, *m*-hydroxy-, *p*-hydroxy-, *o*-chloro- and *p*-dimethylamino-benzaldehydes, *p*-tolualdehyde, anisaldehyde, salicylaldehyde, vanilline, ∝-naphthaldehyde, and β-naphthaldehyde, and *p*-chloro-, 2-hydroxy-5-chloro- and 2-hydroxy-3-chloro-acetophenones with furfuryl aldehyde.



[X=alkyl group; R′=substituted groups]

The chalkones have been prepared by treating different acetophenone, (1.0*M*) with the appropriate benzaldehyde (2.2*M*) in 95% ethanol (25 c.c.) and 50% KOH (50 c.c.). This was thoroughly mixed by shaking and kept for 7 days. Subsequently dilute hydrochloric acid was added and the chalkones separating were crystallised from suitable solvents.

Bromination was carried out in acetic acid medium and the reactivity of the dibromide was examined with potassium iodide. All the dibromides gave the corresponding chalkones from which they were prepared as they did not show any depression in m.p. with the original chalkones (Vanderwalla and Jadhav, this *Jounral*, 1954, **31,** 746).

2,4-Dichlorophenyl acetate was prepared according to Chattaway (*J. Chem. Soc.*, 1931, 2495).

2-*Hydroxy*-3,5-*dichloroacetophenone*.—The Fries rearrangement of the above ester was carried out according to Sen and Bhargava (this *Journal*, 1954, **26,** 368).

Preparation of Chalkones.—To the appropriate acetophenone (1.0*M*), dissolved in 95% ethanol (25 c.c.), different aldehydes (2.2 *M*) were gradually added to it, followed by a 50% solution of KOH (50 c.c.). The solution was well shaken and allowed to stand for 7 days at

the room temperature. The chalkone was obtained by neutralising with HCl (dil.) and recrystallised from glacial acetic acid.

TABLE I

No.	Chalkone.	M.P.	Yield.	%Chlorine.		Dibromide.		%Total halogen.	
				Found.	Calc.	M.P.	Formula	Found.	Calc.
1.	2′-Hydroxy-3′,5′-dichloro-	142°	82%	24.11	24.23	115-16°	$C_{15}H_{10}O_2Cl_2Br_2$	50.90	50.99
2.	2-′Hydroxy-3′,5′-dichloro-4-nitro-	>265°	82	(N)4.09	4.14	160°	$C_{15}H_9O_4NCl_2Br_2$	46.32	46.39
3.	2′,3-Dihydroxy-3′,5′-dichloro-	165°	73	22.90	23.00	210°	$C_{15}H_{10}O_3Cl_2Br_2$	49.21	49.25
4.	2′,4-Dihydroxy-3′, 5′-dichloro-	200-201°	74	22.96	23.00	-	..	..	..
5.	2′-Hydroxy-2,3′,5′-trichloro-	143°	65	32.48	32.52	143°	$C_{15}H_9Cl_3Br$	54.60	54.66
6.	4-Dimethylamino-2′-hydroxy-3′,5′-dichloro-	194°	67	(N)4.14	4.16	110°	$C_{17}H_{15}O_2NCl_2Br_2$	46.52	46.57
7.	4-Methyl-2′-hydroxy-3′, 5′-dichloro-	115°	69	23.10	23.15	160°	$C_{16}H_{12}O_2Cl_2Br_2$	49.40	49.46
8.	4-Methoxy-2′-hydroxy-3′,5′-dichloro-	148°	66	21.90	21.99	85-90°	$C_{16}H_{12}O_3Cl_2Br_2$	47.78	47.82
9.	2′-Hydroxy-3′,5′-dichloro-furfurylidene-	130°	75	25.01	25.09	102°	$C_{13}H_8O_3Cl_2Br_2$	52.12	52.14
10.	2,2′-Dihydroxy-3′,5′-dichloro-	159°	73	22.96	22.97	130°	$C_{15}H_{10}O_3Cl_2Br_2$	49.22	49.25
11.	2,2′-Dihydroxy-3,5′-dichloro-β-naphthylidene-	53°	87	19.62	19.78				
12.	1,2′-Dihydroxy-3′,5′-dichloro-α-naphthylidene-	221°	76	19.62	19.78	95°	$C_{19}H_{12}O_3Cl_2Br_2$	44.50	44.50
13.	2′,4-Dihydroxy-3-methoxy-3′,5′-dichloro-	137°	60	20.89	20.94	210°	$C_{16}H_{12}O_4Cl_2Br_2$	46.23	46.29
14.	4′-Chlorofurfurylidene-	101°	79	15.24	15.27	145°	$C_{13}H_9O_4Cl\ Br_2$	49.80	49.80
15.	2′-Hydroxy-5′-chloro-furfurylidene-	b.p. 200/5mm	73	14.25	14.28	..	..	..	..
16.	2′-Hydroxy-3′-chloro-furfurylidene-	135°	80	14.24	14.28	123°	$C_{13}H_9O_3Cl\ Br_2$	47.80	47.85

Dibromide was prepared by brominating the chalkone in acetic acid medium for one hour with a 10% solution of bromine in acetic acid.

Debromination was done by boiling with an equal weight of potassium iodide in presence of acetone for 4 hours and this led to regeneration of the chalkone.

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CHEMISTRY DEPARTMENT,
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LUCKNOW.

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Colouring Matters of *Matthiola Incana*

D. S. Bhakuni*

From the seeds of *Matthiola incana* (red variety) a mucilage and an oil (Bhakuni and Joshi, *Proc. Nat. Acad. Sci. India*, 1959, **28A**, 1, 190) were isolated and studied earlier. Further chemical examination of the seeds has resulted in the isolation of two crystalline colouring substances, designated provisionally as mathiolin A, m.p. 286°, and mathiolin B, m.p. 263°, respectively.

The defatted seeds, free from mucilage, were extracted according to Bhakuni (*J. Sci. Ind. Res.*, 1961, **20B**, 297) as in the case of the seeds of the yellow variety. The mixture of the colouring matters, thus obtained after purification through organic solvents, when treated with acetone, yielded two fractions, the acetone-insoluble and the acetone-soluble. The former fraction on recrystallisation from glacial acetic acid gave mathiolin A as red plates, m.p. 286°. [Found: C, 60.96; H, 3.89; OMe, 10.22; C-Me, nil. $C_{16}H_{12}O_7$ requires C, 60.76; H, 3.79; OMe (for one), 9.81%]. The latter fraction on repeated purification through acetone-ether and finally on recrystallisation from ethyl acetate gave mathiolin B as orange-red plates, m.p. 263°. [Found: C, 61.87; H, 3.94; OMe, 9.84; C-Me, 4.24. $C_{17}H_{12}O_7$ requires C, 62.19; H, 3.65; OMe (for one), 9.45; C-Me (for one), 4.57%].

Mathiolin A

Mathiolin A dissolves in alkalies to an orange-red solution. It develops a greenish violet colour with H_2SO_4 (conc.) and a greenish colour with ethanolic ferric chloride. Routine analysis of the compound showed the presence of one OMe and the absence of C-Me groups in the molecule.

The compound on acetylation with acetic anhydride-pyridine (at 100°, for 4 hours) formed a tetra-acetate as pale yellow needles (glacial acetic acid), m.p. 165°. [Found: C, 59.34; H, 4.24; OAc, 34.6. $C_{24}H_{20}O_{11}$ requires C, 59.50; H, 4.13; OAc (for four), 35.52%]. With benzoyl chloride-pyridine it formed a tetrabenzoate, m.p. 180-82°. (Found: C, 72.33; H, 3.94. $C_{44}H_{28}O_{11}$ requires C, 72.13; H, 3.82%).

Methylation of mathiolin A with methyl sulphate in dry acetone and in presence of anhydrous potassium carbonate (refluxed for 30 min.) furnished a dimethyl ether in orange-red plates (ethyl acetate), m.p. 198°. (Found: C, 62.89; H, 4.48. $C_{18}H_{16}O_7$ requires C, 62.79; H, 4.65%).

The filtrate obtained after removal of the dimethyl ether, on further treatment with the same quantities of potassium carbonate and methyl sulphate (refluxed for 4 hours), gave a trimethyl ether in orange needles (glacial acetic acid), m.p. 176-77°. (Found: C, 63.42; H, 5.32. $C_{19}H_{18}O_7$ requires C, 63.68; H, 5.02%).

*Present address: National Botanic Gardens, Lucknow.

Mathiolin A on treating with 80% H_2SO_4 (at 100°, for 2 hours) gave a demethoxylated compound as orange-red plates, m.p. 270°. (Found: C, 59.82; H, 3.50. $C_{15}H_{10}O_7$ requires C, 59.60; H, 3.31%).

The compound on distillation with zinc dust furnished a colorless compound (ethanol), m.p. 204°, which showed no depression on admixture with an authentic sample of 2-methylanthracene.

The studies carried out so far on mathiolin A indicates that the compound is an anthraquinone derivative, having four hydroxyl groups out of which three are phenolic in nature and the one, which escapes methylation, appears to be alcoholic in function. It also contains one OMe group.

Mathiolin B

Mathiolin B gave an orange-coloured solution with caustic alkalies, a greenish colour with H_2SO_4 (conc.), and a violet colour with ethanolic ferric chloride. Its reaction with sodium bicarbonate indicated the presence of a carboxyl function in the molecule. Routine analysis of the compound showed the presence of one C-Me and OMe groups in the molecule.

With acetic anhydride-pyridine it formed a diacetate in yellow plates (glacial acetic acid), m.p. 176°. [Found: C, 61.02; H, 4.18; OAc, 20.32. $C_{21}H_{16}O_9$ requires C, 61.16; H, 3.88; OAc (for two), 20.87%].

The compound on methylation (in the similar manner as in case of mathiolin A) formed a monomethyl ether, m.p. 166°. (Found: C, 63.35; H, 4.18. $C_{18}H_{14}O_7$ requires C, 63.15; H, 4.09%] and a dimethyl ether, m.p. 152-53°. (Found: C, 64.26; H, 4.38. $C_{19}H_{16}O_7$ requires C, 64.04; H, 4.49%).

Demethoxylation of mathiolin B with 80% H_2SO_4 (at 100° for 2 hours) gave orange-red plates (glacial acetic acid), m.p. 253°. [Found: C, 60.84; H, 3.36. $C_{16}H_{10}O_7$ requires C, 61.14; H, 3.18%).

Mathiolin B on distillation with zinc dust in a stream of hydrogen furnished colorless leaflets (ethanol), m.p., 205°, which showed no depression on admixture with an authentic sample of 2-methylanthracene.

The experimental data given above suggest that mathiolin B is also an anthraquinone derivative having a C-Me group in 2-position of the basic anthraquinone nucleus. It also contains a C-Me, a carboxyl and two phenolic hydroxyl groups in the molecule. Further study of these compounds is in progress.

Chemical Laboratories,
University of Allahabad,
Allahabad.

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Micro-precipitation Equipment for the Use of Potassium Trithiocarbonate as the Cation-precipitant

K. N. Johri

The overall superiority of potassium trithiocarbonate reagent (Johri, *J. Sci. Ind. Res.*, 1958, **17B**, 333; 1959, **18B**, 430) over hydrogen sulphide and thioacetamide (Blomendal and Veer Kamp, *Chem. Weekbl.*, 1953, **49**, 147; Lehrman and Schneider, *J Chem. Ed.*, 1955, **32**, 474) as cation-precipitant has made possible to extend its application to micro-analysis with great advantages.

Treatment of test solutions in micro-analysis with hydrogen sulphide obtained from a U-tube micro-generator (Sorum, "Introduction to Semimicro Analysis") fitted with a jet delivery tube and a spring-clip has proved far from satisfactory. Besides the undue leakage of the gas and the contamination of laboratory atmosphere, frequent blocking of the jet delivery-tube of the generator results due to the capillary suction of a test solution and its consequent precipitation within the jet. To avoid this, a high pressure ejection of the gas from the jet becomes necessary before it is either inserted into the test solution or withdrawn from it. This results in the leakage of the gas in a greater degree and also in the sputtering of the test solution.

On the other hand, while using potassium trithiocarbonate reagent and the 'micro-precipitation equipment', the above noted difficulties are successfully overcome. As an additional advantage, the products of precipitation are obtained in highly coagulated form, necessitating only minimum centrifuging in the case of such cations of which the products of precipitation tend to become colloidal. Cadmium is prominent in this respect, as in low concentration its sulphide tends to become colloidal. Furthermore, the use of potassium trithiocarbonate makes possible the application of the new technique, called "precipitation from homogeneous solution". Under this technique the precipitating agent is not added as such, but is generated within the solution by a chemical reaction. In the case of the thiocarbonate reagent, it is the thiocarbonic acid or hydrogen sulphide, which is generated, depending on the *p*H at a stage.

Equipment and Procedure

This apparatus, as represented in Fig 1, has been made with quick-fit joints out of pyrex parts. It is meant to carry out precipitation of minute quantities of inorganic materials

as sulphides or thiocarbonates, depending on the *p*H of the test solutions. This will accomplish the clean separation of the cations without causing any sputtering or leakage of any toxic gas. The conical enclosure forms the main body of the set-up in which a micro-beaker (M) or a centrifuge-tube (T) containing the test solution is lodged firmly in position with the help of glass stopper (Fig. 1a) or a rubber cork (Fig. 1b) holding the tube.

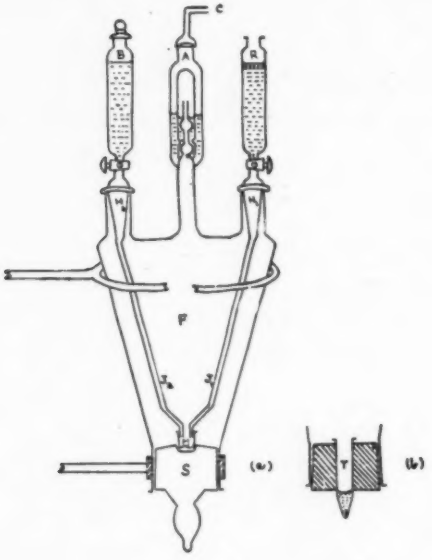

FIG. 1.

The dropping funnel (B), provided with a long narrow stem and a stop cock, holds nearly 0.25*N*-HCl. The second dropping funnel (R) is meant to deliver in drops the trithiocarbonate reagent to a test solution for preciptation. The part (A) is charged with a dilute solution of KOH through which any liberated hydrogen sulphide bubbles and is trapped, the residual gas being completely drawn out of (F) by connecting (C) to a filter pump while stopper (S) is slightly loosened in the end to admit air from below. This is done before withdrawing the micro-beaker or the centrifuge tube after each precipitation. While adding the thiocarbonate reagent to a test-solution, the end of the jet (J_1) is moved by rotating (H_1) so as to touch the side of the microbeaker or the centrifuge tube. Same procedure is adopted when the acid from (B) is added for the subsequent treatment of group II metal sulphides. A protective layer of liquid paraffin, kept over the reagent in funnel (R) maintains its purity. When precipitation with the thiocarbonate reagent is complete, the stopper of the bulb (A) is connected to suction line (filter pump) and the stopper (S) carrying the micro-beaker or the rubber cork holding the centrifuge tube is taken out to check the *p*H of the test solution with the help of methyl violet indicator paper. The whole apparatus rests at the same height and clampled vertically, as shown in Fig. 1. The bulb (A) is periodically emptied and after washing with water it is recharged with a fresh dilute solution of KOH. Potassium hydrogen sulphide collected from (A) can be subsequently utilised in the preparation of the trithiocarbonate reagent.

Characteristic Features of the New Scheme as Adapted to Micro-analysis

For the clean separation of group II metals including cobalt, present in minute amounts, optimum *p*H range required is 0.5 to 0.7, which is adjusted with methyl violet indicator (*p*H range 0.1-2.0) paper-strip turning green. The strip is finally washed clean of any adhering portion of the test solution. In practice, it is found advantageous to add the thiocarbonate reagent always in slight excess (green to blue tint) so as to ensure complete precipitation of the group. This may result in the formation of some soluble complex thiocarbonates of copper, cobalt, and the amphoteric arsenic, antimony and tin. To reprecipitate these, gradual acidification with more of dilute hydrochloric acid is required (blue to green tint). This procedure for microchemical analysis requires the concentration of the thiocarbonate reagent not more than 0.8% and that of HCl as 0.2*N* to 0.25*N*. This will obviate separation of free sulphur and help in the adjustment of *p*H. To avoid the separation of free sulphur on account of the presence of oxidising anions like dichromate, permanganate, and arsenate, prior reduction of these with a few drops of 10% farmaldehyde is advantageous when chromium, manganese, and arsenic salts respectively are produced. Evaporation of the solution on the micro water bath almost to dryness is, however, found necessary before adjusting the *p*H for precipitating group II metals.

Coupled with the technique of 'extraction analysis' using organic solvents for isolation of a metal from the allied ones of a group, the use of the thiocarbonate reagent would enhance the efficiency of the colorimetric tests for metals present in minute amounts.

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CHEMICAL LABORATORIES,
UNIVERSITY OF DELHI,
DELHI-6.

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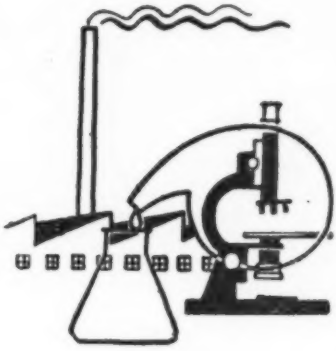

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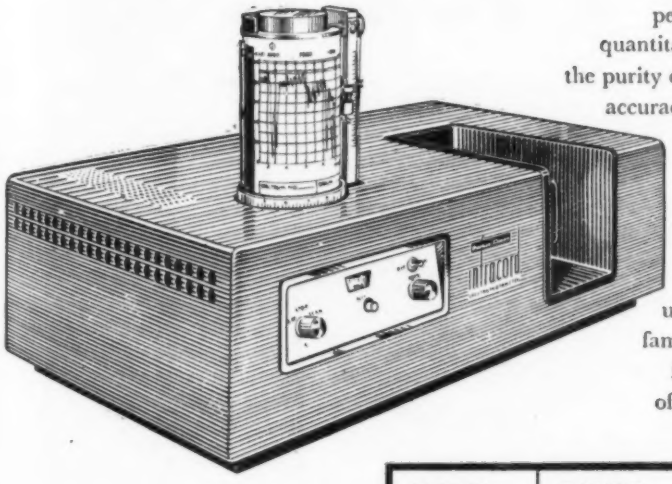

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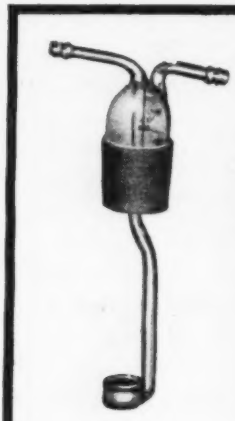

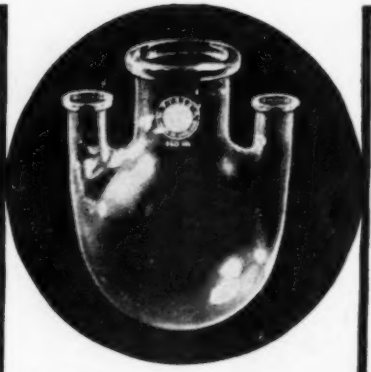

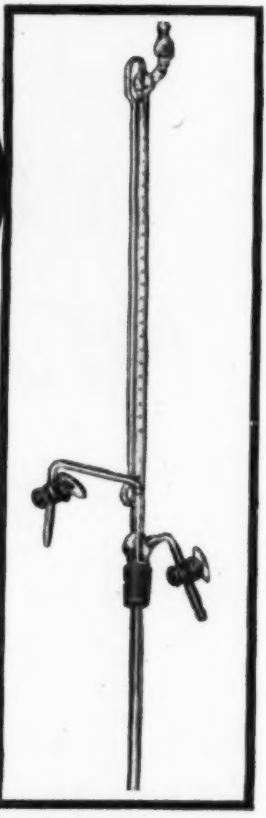

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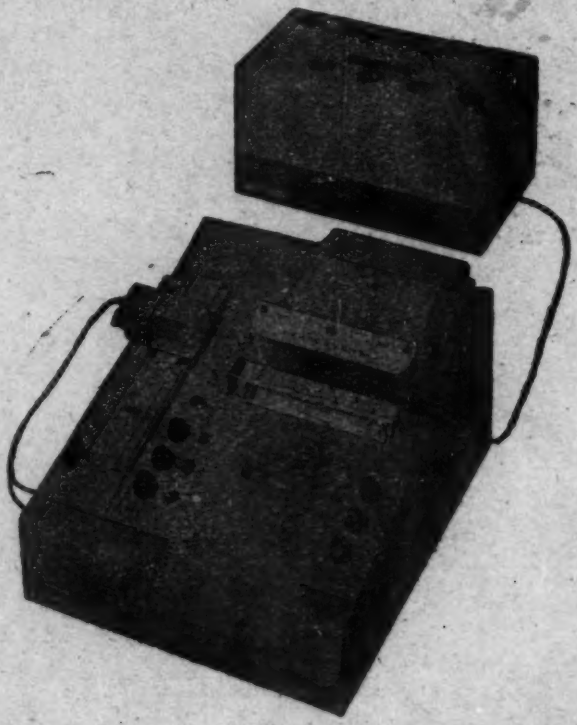

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